



(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention  
of the grant of the patent:  
07.10.1998 **Bulletin** 1998/41

(51) Int Cl.<sup>6</sup> **C08F 10/00**, C08F 4/646,  
C08F 4/647

(21) Application number. 91913096.3

(86) International application number:  
**PCT/JP91/00983**

(22) Date of filing: **24.07.1991**

(87) International publication number:  
**WO 92/01723 (06.02.1992 Gazette 1992/04)**

**(54) CATALYST FOR ALPHA-OLEFIN POLYMERIZATION AND PRODUCTION OF  
POLY-ALPHA-OLEFIN THEREWITH**

KATALYSATOR FÜR ALPHA-OLEFINPOLYMERISATION UND HERSTELLUNG VON  
POLY(ALPHA)OLEFINEN DAMIT

CATALYSEUR POUR POLYMERISATION ALPHA-OLEFINIQUE ET PRODUCTION D'UNE  
POLY-ALPHA-OLEFINE A L'AIDE DE CE CATALYSEUR

(84) Designated Contracting States:  
**BE DE FR GB IT NL**

(30) Priority: 24.07.1990 JP 193904/90  
01.08.1990 JP 202455/90  
27.08.1990 JP 222582/90  
02.10.1990 JP 262985/90  
13.11.1990 JP 303791/90  
13.11.1990 JP 303792/90  
08.02.1991 JP 17371/91  
12.02.1991 JP 18531/91  
13.02.1991 JP 19792/91  
13.02.1991 JP 19793/91  
21.02.1991 JP 27056/91  
13.03.1991 JP 47851/91  
13.03.1991 JP 47984/91

(43) Date of publication of application:  
**02.09.1992 Bulletin 1992/36**

(60) Divisional application: **98102883.0 / 0 841 349**

(73) Proprietor: **MITSUI CHEMICALS, INC.**  
**Tokyo (JP)**

(72) Inventors:

- **SUGIMOTO, Ryuchi**  
Takaishi-shi, Osaka 592 (JP)
- **ASANUMA, Tadashi**  
Takaishi-shi, Osaka 592 (JP)
- **IWATANI, Tutomu**  
Takaishi-shi, Osaka 592 (JP)
- **TAKEUCHI, Katsumi**  
Takaishi-shi, Osaka 592 (JP)
- **UCHIDA, Osamu**  
Takaishi-shi, Osaka 592 (JP)

(74) Representative:

Luderschmidt, Schüler & Partner GbR  
Patentanwälte,  
Postfach 3929  
65029 Wiesbaden (DE)

(56) References cited:

JP-A- 1 301 704	JP-A- 1 501 950
JP-A- 1 502 036	JP-A-61 130 314

## Description

## Technical Field

5 The present invention relates to a polymerization catalyst for an  $\alpha$ -olefin and a method for preparing a poly- $\alpha$ -olefin by the use of the same. More specifically, it relates to a novel catalyst system using a halogenated metallocene compound and a method for preparing a poly- $\alpha$ -olefin by the use of this catalyst in a high activity per unit amount of the catalyst.

## 10 Background Art

A known polymerization catalyst for an olefin comprises a combination of a metallocene compound having a group with conjugated pi-electrons, particularly cyclopentadiene and its derivative as ligands and an alkylaluminoxane obtained by the reaction of trialkylaluminum and water. For example, Japanese Patent Application Laid-open No. 19309/1983 discloses a polymerization process of an olefin by the use of a catalyst composed of bis(cyclopentadienylzirconium dichloride and methylaluminoxane. Furthermore, Japanese Patent Application Laid-open Nos. 130314/1986, 264010/1986, 301704/1989 and 41303/1990 disclose preparation methods of isotactic poly- $\alpha$ -olefins or syndiotactic poly- $\alpha$ -olefins and polymerization catalysts which can be used to prepare these poly- $\alpha$ -olefins having a steric regularity, but the disclosed catalysts all utilize aluminoxanes as co-catalysts.

15 On the other hand, researches have heretofore been made into an aluminoxane-free homogeneous Ziegler-Natta catalyst system, and it has been known that this kind of catalyst has a polymerization activity for olefins, though this activity is low. The active species of this catalyst is considered to be a cationic metallocene compound or an ion pair type metallocene complex.

20 In recent years, it has been reported that an isolated cationic metallocene compound having cyclopentadiene or its derivative as a ligand can singly exert the polymerization activity for olefins, even if methylaluminoxane as the co-catalyst does not coexist.

25 For example, in R. F. Jordan et al., J. Am. Chem. Soc., Vol. 108, 1986, p. 7410-7411, it has been reported that a zirconium cationic complex having tetraphenylborane as an anion and having two cyclopentadienyl groups and a methyl group as ligands can be isolated by utilizing a donor such as tetrahydrofuran as a ligand, and the isolated complex exerts a polymerization activity for ethylene in methylene chloride.

30 Furthermore, Turner et al. have reported in J. Am. Chem. Soc., Vol. 111, 1989, p. 2728-2729, Japanese Patent Disclosure (Kohyo) Nos. 501950/1989 and 502036/1989 that an ion pair type metallocene complex has a polymerization activity for olefins, and this type of metallocene complex is composed of a metallic compound having a cyclopentadienyl group or its derivative as a ligand containing at least one substituent capable of reacting with a proton and a compound which has a cation capable of donating the proton and which can feed a stable anion. In Zambelli et al., Macromolecules, Vol. 22, 1989, p. 2186-2189, it has been reported that propylene is polymerized with the aid of a catalyst comprising the combination of a zirconium compound having a derivative of a cyclopentadienyl group as a ligand, trimethylaluminum and fluorodimethylaluminum to obtain an isotactic polypropylene. Also in this case, the active species is considered to be the ion pair type metallocene compound.

35 In addition, Marks et al. have reported in Langmuir, Vol. 4, No. 5, 1988, p. 1212-1214 that a catalyst supporting a dimethylzirconium complex having a cyclopentadienyl derivative as a ligand on alumina completely dehydrated by a heat treatment at about 1000°C exerts a polymerization activity for ethylene. This catalyst system is also considered to be a cationic metallocene compound. However, in the connected column of the literature, the description regarding ethylene is seen, but any  $\alpha$ -olefin is not referred to.

40 The polymerization methods of olefins by the use of a catalyst comprising the combination of the metallocene compound and the alkylaluminoxane disclosed in Japanese Patent Application Laid-open No. 19309/1983 have the feature that the polymerization activity per unit of a transition metal is high. However, in these methods, the polymerization activity per unit of the metallocene compound is high, but the expensive aluminoxane is used in large quantities, and therefore the polymerization activity per unit of the aluminoxane is not so high. In consequence, there is the problem that the production cost of the polymer is high and the other problem that after the polymerization, the removal of the aluminoxane from the produced polymer is very difficult and a large amount of the catalyst residue remains in the polymer.

45 On the other hand, in the methods of R. F. Jordan et al. and Turner et al., no alkylaluminoxane is used and the cationic zirconium complexes are utilized as the catalysts. Therefore, the above-mentioned problem regarding the alkylaluminoxane is not present. However, the polymerization activity of these catalysts is much lower as compared with that of the catalyst systems using the alkylaluminoxane and most of the complex catalysts cannot polymerize  $\alpha$ -olefins having 3 or more carbon atoms. Furthermore, these methods require a dimethyl complex which can be obtained by alkylating a dichloro complex with an expensive alkylating agent such as methyl lithium or a methyl Grignard reagent,

and they have the problem regarding the yield of the alkylation, which increases the production cost of the catalysts. In addition, these alkylated metallocene compounds are unstable, and in particular, their solutions in a hydrocarbon solvent or the like easily decompose owing to a trace amount of impurities such as water and oxygen, or light. Accordingly, it is difficult to store the catalysts in the state of the solution, and thus each metallocene solution must be prepared afresh before the polymerization. Moreover, at the time of the polymerization, the contamination of the monomer and the solvent with the impurities must be inhibited to the utmost. In the case that an olefin is polymerized by the use of the Ziegler system catalyst, the impurities can be removed from the monomer and/or the solvent by treating the same with an organometallic compound, particularly an alkylaluminum compound. This removal manner can be applied to the case where the ion pair system catalyst is used, and when the monomer and/or the solvent which has been treated with the alkylaluminum is employed, the polymerization activity of the catalyst for the olefin is improved to some extent, but nevertheless, this activity is poorer as compared with the combined catalyst system using the alkylaluminoxane as the co-catalyst. In the method of Zambelli et al., propylene is polymerized with the aid of the catalyst system comprising trimethylaluminum, dimethylaluminum fluoride and the zirconium complex to obtain an isotactic polypropylene, as described above, and the expensive aluminoxane and the dimethyl complex are not used. However, in this kind of catalyst, the organometallic compound containing fluorine is used and the polymerization activity is extremely low. This polymerization activity can be slightly improved by using a halogenated hydrocarbon such as methylene chloride as the reaction solvent, but nevertheless it is still low, and the halogenated hydrocarbon, since being poisonous, is not preferable as the solvent.

#### 20 Disclosure of the Invention

The present inventors have intensively researched on a stable catalyst system by which the above-mentioned problems can be solved and by which an  $\alpha$ -olefin can be polymerized with a high activity without using an alkylaluminoxane, and as a result, the present invention has been completed. That is, the present invention is directed to a method for polymerizing an  $\alpha$ -olefin characterized by using a catalyst system which can be obtained by reacting a halogenated metallocene compound with an organometallic compound, and then bringing the resultant reaction product into contact with an ionic compound or an electrophilic compound.

#### Brief Description of the Drawings

30 Fig. 1 shows a proton NMR spectrum of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride.  
 Fig. 2 shows a proton NMR spectrum measured 10 minutes after isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was mixed with triethylaluminum, and in Fig. 2, (a) is a general view and (b) is a partially enlarged view.  
 Fig. 3 shows a proton NMR spectrum measured 10 minutes after isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was mixed with trimethylaluminum.  
 Fig. 4 shows a proton NMR spectrum measured after isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was mixed with trimethylaluminum and the resultant mixture was then allowed to stand for 240 hours.  
 Fig. 5 shows a proton NMR spectrum of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dimethyl complex.  
 The halogenated metallocene compound of a catalyst system which is used in the present invention is a compound 40 represented by the formula (I) or (II)

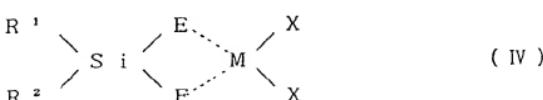


55 wherein A and B or A' and B' may be mutually identical or different and they are unsaturated hydrocarbon residues



Other examples of the halogenated metallocene compound represented by the formula (II) include the divalent groups in which the ethylene group in a crosslinked portion is replaced with an isopropylidene group, a cyclopentadiene group, a cyclohexylidene group, a methylphenylmethylen group, a diphenylmethylen group, a 1,4-cyclopentane-di-ylidene group, a 1,4-cyclohexane-di-ylidene group, a dimethylgermylene group or a dimethylstanylene group. Additional examples include similar complexes in which the zirconium atom is replaced with a titanium atom or a hafnium atom and similar complexes in which the chloride is replaced with a bromide, an iodide or a fluoride.

An example of the halogenated metallocene compound which can be used in the present invention is a compound represented by the formula (IV).



55 wherein each of E and F is a di- or tri-substituted cyclopentadienyl group having a hydrocarbon residue having 1 to 10 carbon atoms, a silyl group or a halogen atom as a substituent; R<sup>1</sup> and R<sup>2</sup> may be identical or different and they are bonded to silicon which is linked with the two cyclopentadienyl groups, and each of R<sup>1</sup> and R<sup>2</sup> is a hydrogen atom or a hydrocarbon residue having 1 to 10 carbon atoms; M is a titanium atom, a zirconium atom or a hafnium atom; and X is a halogen atom.

Each example of E and F is a di- or tri-substituted cyclopentadienyl group in which a part of the hydrogen atoms

is replaced with hydrocarbon residues having 1 to 10 carbon atoms, silyl groups or halogen atoms.

Each of R<sup>1</sup> and R<sup>2</sup> is the substituent bonded to silicon which is linked with the two cyclopentadienyl groups, and each example of R<sup>1</sup> and R<sup>2</sup> is a hydrogen atom or a hydrocarbon residue having 1 to 10 carbon atoms such as methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopentyl, cyclohexyl or phenyl. Furthermore, they may be identical or different.

5 An example of X is a fluorine atom, a chlorine atom, a bromine atom or an iodine atom.

Typical examples of the halogenated metallocene compound represented by the formula (IV) are as follows:

Dimethylsilylenebis(3-methylcyclopentadienyl)-zirconium dichloride, dimethylsilylenebis(2,4-dimethylcyclopentadienyl)zirconium dichloride, dimethylsilylenebis(2,4-diethylcyclopentadienyl)zirconium dichloride, dimethylsilylenebis(2,3,5-trimethylcyclopentadienyl)zirconium dichloride, dimethylsilylenebis(2,4-di-t-butylcyclopentadienyl)zirconium dichloride, dimethylsilylenebis(phenylcyclopentadienyl)zirconium dichloride, dimethylsilylenebis(3-ethylcyclopentadienyl)zirconium dichloride, dimethylsilylenebis(2,4-diphenylcyclopentadienyl)zirconium dichloride, dimethylsilylenebis(2,3,5-triethylcyclopentadienyl)zirconium dichloride, dimethylsilylenebis(3-isopropylcyclopentadienyl)zirconium dichloride, dimethylsilylenebis(3-phenylpropylcyclopentadienyl)zirconium dichloride, dimethylsilylenebis(3-t-butylcyclopentadienyl)zirconium dichloride, dimethylsilylene(methylcyclopentadienyl)(2,4-dimethylcyclopentadienyl)zirconium dichloride, dimethylsilylene(2,4-dimethylcyclopentadienyl)(2,3,5-trimethylcyclopentadienyl)zirconium dichloride, dimethylsilylene(cyclopentadienyl)(tetramethylcyclopentadienyl)zirconium dichloride, dimethylsilylene(2,4-dimethylcyclopentadienyl)(3-ethylcyclopentadienyl)zirconium dichloride, dimethylsilylene(2,4-dimethylcyclopentadienyl)(2,4-diethylcyclopentadienyl)zirconium dichloride, dimethylsilylene(methylcyclopentadienyl)(2,3,5-trimethylcyclopentadienyl)zirconium dichloride, dimethylsilylene(methylcyclopentadienyl)(t-butylcyclopentadienyl)zirconium dichloride and dimethylsilylene(methylcyclopentadienyl)(phenylcyclopentadienyl)zirconium dichloride. Additional examples of the halogenated metallocene compound represented by the formula (IV) include similar compounds in which the dimethylsilylene group is replaced with a methylphenylsilylene group, a diethylsilylene group, a diphenylsilylene group, an ethylphenylsilylene group, a dipropylsilylene group and a dibenzylsilylene group. Other examples of the halogenated metallocene compound represented by the formula (IV) include similar complexes in which the zirconium atom is replaced with a titanium atom or a hafnium atom, and similar complexes in which the chloride is replaced with a bromide, an iodide and a fluoride.

The organometallic compound with which the halogenated metallocene compound is treated is triethylaluminum, tripropylaluminum, triisopropylaluminum, tributylaluminum, triisobutylaluminum, triptyylaluminum, trihexylaluminum, triheptylaluminum, trioctylaluminum, trimethylaluminum, isopropylaluminum, diethylaluminum hydride, diisopropylaluminum hydride, diisobutylaluminum hydride, diethylzinc, diphenylzinc, divinylzinc, dimethylmagnesium, diethylmagnesium, dibutylmagnesium, dihexylmagnesium or butylethylmagnesium.

No particular restriction is put on the process for treating the halogenated metallocene compound with the organometallic compound, and this treatment can be achieved by merely mixing both the materials. In general, the halogenated metallocene compound is in a solid state and the organometallic compound is often in a liquid or a solid state, and so the above-mentioned treatment is preferably carried out in a hydrocarbon solvent. Examples of this hydrocarbon solvent include saturated hydrocarbon compounds such as propane, butane, isobutane, pentane, hexane, heptane, octane, nonane, decane, cyclopentane, cyclohexane, cycloheptane and methylcyclohexane; and aromatic hydrocarbon compounds such as benzene, toluene and xylene.

40 The solubility of the halogenated metallocene compound in the hydrocarbon solvent is usually very low, but when the organometallic compound is added thereto and the above-mentioned treatment is then carried out, the reaction product from the halogenated metallocene compound contacted with the organometallic compound is readily soluble in the hydrocarbon solvent, and even if it has a high concentration, a homogeneous solution can be obtained. It has been preferably found that the reaction product of the halogenated metallocene compound and the organometallic compound is very stable to light, heat and a small amount of impurities in the hydrocarbon solvent. The reaction product in the hydrocarbon solvent is extremely stable in contrast to the fact that an alkylmetallocene compound obtained by alkylating the halogenated metallocene compound with an alkylating agent is unstable in the hydrocarbon solvent. Therefore, even if the solution is stored for a long period of time, the metallocene compound does not decompose to produce insolubles and the activity of the reaction product as the polymerization catalysts for olefins neither deteriorates nor disappears, and thus the reaction product can stably be stored for a long time. The characteristics of the reaction product obtained by this reaction have not been elucidated so far, but it is definite from the difference of the stability in the hydrocarbon solvent that the alkylmetallocene compound obtained by alkylating the halogenated metallocene compound with the aid of the organometallic compound is not merely present in the reaction product. For example, Kaminsky et al. have reported in Liebigs Ann. Chem., 1975, p. 424-437 that the reaction of dicyclopentadienylzirconium dichloride as the halogenated metallocene compound and triethylaluminum compound as the organometallic compound produces about 10 kinds of products. Furthermore, E. Negishi et al. have reported in Tetrahedron Lett., Vol. 27, 1986, p. 2829 that the dialkylmetallocene compound having an alkyl group of 2 or more carbon atoms cannot be stored stably at room temperature and it decomposes to produce "ZIRCONOCENE". As described above, the reaction product

obtained by treating the halogenated metallocene compound with the organometallic compound has not been elucidated in the structure thereof so far, but it becomes a highly active species when used as the polymerization catalysts for  $\alpha$ -olefins, in contrast to the alkylmetallocene compound.

It has been known that in the case that an  $\alpha$ -olefin is polymerized by the use of a conventional alkylmetallocene compound, catalytic activity does not start immediately, even when the metallocene compound is brought into contact with a compound which will become a stable anion, and a long induction time of 1 to 15 minutes or more is taken and afterward the polymerization reaction begins vigorously. However, in the case that the product obtained by treating the halogenated metallocene compound with the organometallic compound is used to polymerize the  $\alpha$ -olefin as in the present invention, such a phenomenon is not be observed, and immediately when the above-mentioned product is brought into contact with the compound which will become a stable anion, the polymerization reaction begins. This is considered to be attributable to the fact that the activator of the present invention is different from the activator formed by using the alkylmetallocene compound.

The amount of the organometallic compound is normally from 1 to 1000 mols, preferably from 2 to 500 mols per mol of the halogenated metallocene compound. No particular restriction is put on a treatment temperature, but in general, the treatment is preferably carried out at a temperature of from -20 to 100°C. Furthermore, no particular restriction is put on a temperature at which a mixture thereof is stored, but it is preferred that the mixture is stored at the same temperature of from -20 to 100°C.

No particular restriction is put on a treatment time, and if both of the materials are in a solution state, the treatment time is a time until they have been uniformly mixed. If insolubles are present, they should be dissolved in the solvent, and after they have been completely dissolved, the mixture can be used at any time. Needless to say, the mixture may be beforehand prepared and stored until it will be actually used. No particular restriction is put on the concentration of the reaction product in the hydrocarbon solvent, because the reaction product is stable even at the high concentration as described above, but usually the molar concentration of the reaction product is from  $10^{-7}$  to 1 mol per liter, preferably from  $10^{-5}$  to 0.1 mol per liter in terms of the mol of the metallocene compound.

In the present invention, the electrophilic compound is formed from an ion pair of a cation and an anion, and can be reacted with the reaction product of the halogenated metallocene compound and the organometallic compound to become a stable ion and to thereby form the polymerization activator. The ionic compound is represented by the formula (V).

30



Q is a cationic component of the ionic compound, and its examples include carbonium cation, tropylium cation, ammonium cation, oxonium cation, sulfonium cation and phosphonium cation. Additional examples include cations of metals and cations of organometals which are easily reduced. These cations may be not only cations capable of providing protons as disclosed in Japanese Patent Disclosure (Kohyo) No. 501950/1989 but also cations which cannot provide the protons. Typical examples of these cations include triphenylcarbenium, diphenylcarbenium, cycloheptatrienylum, indenium, triethylammonium, tripropylammonium, tributylammonium, N,N-dimethyllanilinium, dipropylammonium, dicyclohexylammonium, triphenylphosphonium, trimethylsulfonium, tris(dimethylphenyl)phosphonium, tris(methylphenyl)phosphonium, triphenylsulfonium, triphenyloxonium, triethylloxonium, pyrlyium, silver ion, gold ion, platinum ion, copper ion, palladium ion, mercury ion and ferrocenium ion.

In the above-mentioned formula (V), Y is an anionic component of the ionic compound and it is the component which will be the stable anion when reacted with the reaction product of the halogenated metallocene compound and the organometallic compound. Examples of Y include the anionic components of ionic compounds such as an ionic organoboron, organoaluminum, organogallium, organophosphorus, organoarsenic and organoantimony. Typical examples of Y and the ionic compounds include tetraphenylboron, tetrakis(3,4,5-trifluorophenyl)boron, tetrakis(3,5-di(trifluoromethyl)phenyl)boron, tetrakis(3,5-di(t-butyl)phenyl)boron, tetrakis(pentafluorophenyl)boron, tetraphenylaluminum, tetrakis(3,4,5-trifluorophenyl)-aluminum, tetrakis(3,5-di(trifluoromethyl)phenyl)aluminum, tetrakis(3,5-di(t-butyl)phenyl)aluminum, tetrakis(pentafluorophenyl)aluminum, tetrakis(3,4,5-trifluorophenyl)gallium, tetrakis(3,5-di(trifluoromethyl)phenyl)gallium, tetrakis(3,5-di(t-butyl)phenyl)gallium, tetrakis(pentafluorophenyl)gallium, tetraphenylphosphorus, tetrakis(pentafluorophenyl)phosphorus, tetraphenylarsenic, tetrakis(pentafluorophenyl)arsenic, tetraphenylantimony, tetrakis(pentafluorophenyl)antimony, decaborate, undecaborate, carbadodecaborate and decachlorodecaborate.

The electrophilic compound is a compound which is known as a Lewis acid compound and which will constitute a polymerization active species by forming a stable anion when reacted with the reaction product of the halogenated metallocene compound and the organometallic compound. Examples of the electrophilic compound include various halogenated metallic compounds and metallic oxides known as solid acids. Typical examples of the electrophilic com-

5 pound include magnesium halides and inorganic oxides having Lewis acidity.

6 Examples of the magnesium halides which can be used in the present invention include magnesium compounds  
7 having at least one halogen atom in each molecule, for example, magnesium chloride, magnesium bromide, magnesium iodide, magnesium chlorobromide, magnesium chloroiodide, magnesium bromoiodide, magnesium chloride hydride, magnesium chloride hydroxide, magnesium bromide hydroxide, magnesium chloride alkoxide and magnesium bromide alkoxide.

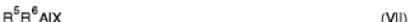
8 The useable magnesium halide has a surface area of from 1 to 300 m<sup>2</sup>/g, and in general, the commercially available  
9 magnesium halides having a surface area of from 1 to 25 m<sup>2</sup>/g can also be used directly. It is more preferable that the  
10 magnesium halide is treated by grinding so that the surface area thereof may be from 30 to 300 m<sup>2</sup>/g. Here, "the surface  
11 area" means a specific surface area measured by utilizing nitrogen molecules as adsorptive molecules in accordance  
12 with a BET multi-point process by the use of a high-speed specific surface area/pore distribution measuring device  
13 ASAP-2000 made by Shimadzu Seisakusho Ltd.

14 The magnesium halide compound having a surface area of from 30 to 300 m<sup>2</sup>/g can be obtained by further grinding  
15 the usually commercially available product having a surface area of 25 m<sup>2</sup>/g or less or by once dissolving the commercial  
16 product and precipitating it again. Furthermore, the magnesium halide can be also synthesized by adding a halogenating  
17 agent to an organomagnesium compound. This typical synthesis can be achieved only by adding, to the solution  
18 of the organomagnesium compound, a halogenating agent which is capable of forming a halogenated magnesium  
19 compound when reacted with the organomagnesium compound. Examples of the organomagnesium compound which  
20 can be here used include dialkylmagnesiums such as dimethylmagnesium, diethylmagnesium, dibutylmagnesium, di-  
21 hexylmagnesium and butylethylmagnesium; diarylmagnesiums such as diphenylmagnesium and bis(triphenylmethyl)-  
22 magnesium; and Grignard reagents such as methylmagnesium bromide, ethylmagnesium chloride, ethylmagnesium  
23 bromide, butylmagnesium chloride, butylmagnesium bromide, butylmagnesium iodide, phenylmagnesium chloride,  
24 phenylmagnesium bromide, cyclohexylmagnesium chloride, naphthylmagnesium bromide and styrylmagnesium bro-  
25 mide. Examples of the compound with which the above-mentioned organomagnesium compound is halogenated in-  
26 clude organic halides such as carbon tetrachloride, chloroform, dichloromethane, carbon tetrabromide, iodofrom, di-  
27 bromomethane, isopropyl chloride, isobutyl chloride, benzyl chloride, triphenyl chloride, isopropyl bromide, isobutyl  
28 iodide, benzyl bromide, triphenyl iodide, benzyl dichloride and benzyl trichloride; inorganic chlorides such as hydrogen  
29 chloride, hydrogen bromide, hydrogen iodide, boron chloride, aluminum chloride, titanium chloride, vanadium chloride,  
30 silicon tetrachloride, phosphorus chloride and thionyl chloride; and halogens such as fluorine, chlorine, bromine and  
iodine.

31 In synthesizing the magnesium halide by adding the halogenating agent to the organomagnesium compound, an  
32 organomagnesium compound represented by the following formula (VI) may be reacted with an organoaluminum com-  
33 pound represented by the following formula (VII) as the halogenating agent in a polymerization vessel to produce the  
34 magnesium halide, i.e., the compound which will be the stable anion in situ, and the  $\alpha$ -olefin can be then polymerized:



35 (wherein R<sup>3</sup> is a hydrocarbon residue having 1 to 20 carbon atoms, and R<sup>4</sup> is a hydrocarbon residue having 1 to 20  
36 carbon atoms or a halogen atom), and



45 (wherein R<sup>5</sup> and R<sup>6</sup> may be identical or different and each of them is a hydrocarbon residue having 1 to 20 carbon  
atoms, an alkoxy group, a halogen atom, an oxygen atom or a hydrogen atom; and X is a halogen atom).

46 In this case, the organomagnesium compound and the organoaluminum compound can both be used as the or-  
47 ganometallic compounds for treating the halogenated metallocene compound, and therefore when the halogenated  
48 metallocene compound is treated with the organomagnesium compound or the organoaluminum compound, the or-  
49 ganometallic compound can be excessively used to react the organoaluminum compound or the organomagnesium  
50 compound with the excess organomagnesium compound or organoaluminum compound in situ, thereby producing the  
51 halogenated magnesium compound, i.e., the compound which will be the stable anion.

52 That is, an excess amount of the organomagnesium compound or the organoaluminum compound as the orga-  
53 nometallic compound with which the halogenated metallocene compound is treated is introduced into the polymeriza-  
54 tion vessel, and the organoaluminum compound or the organomagnesium compound is further added thereto, whereby  
55 the halogenated magnesium can be produced in the polymerization vessel and thus the olefin can be polymerized.

As the inorganic oxide having Lewis acidity which can be used in the present invention, there can usually be used

an inorganic oxide which is commercially available as a solid acid. Examples of the inorganic oxide include silica, alumina, silica-alumina and silica-magnesia. Above all, alumina and silica-magnesia are preferably used. The good inorganic oxides contain no water and have the largest possible surface area, and usually it is preferable to use the compound of a surface area of from 10 to 500 m<sup>2</sup>/g. The particularly preferable compound is aluminum oxide having a surface area of from 15 to 500 m<sup>2</sup>/g. These values of the surface area are what have been measured by the same manner as in the case of the halogenated magnesium compound. When the inorganic oxide having a surface area of 10 m<sup>2</sup>/g or less is used, a sufficient activity cannot be obtained. It is difficult to obtain the compound having a surface area of 500 m<sup>2</sup>/g or more, and even if the surface area is further increased, performance is not so effectively improved any more. Moreover, it is necessary that the inorganic oxide is beforehand dehydrated. As techniques for dehydrating the inorganic oxide, there are a process which comprises subjecting the oxide to a heat treatment at a temperature of from 200 to 1000°C, and another process which comprises additionally dehydrating the oxide with an organometallic compound after the heat treatment. Examples of the organometallic compound which can be used in the dehydration treatment include compounds of metals such as aluminum, zinc and magnesium. In the organometallic compound, a halogen atom, an oxygen atom, a hydrogen atom or a residue such as alkyl, alkoxy or aryl is bonded to a metallic atom, and in the case that the plural members of the latter atoms and residues are used, they may be identical or different, but at least one of them should be the alkyl group. For example, there can be utilized an alkylmetal compound having one or more alkyl residue of 1 to 12 carbon atoms, an alkylmetal halide, or an alkylmetal alkoxide having the above-mentioned alkyl residue and another atom or residue.

The amount of the ionic compound normally from 1 to 100 mols, preferably 1 to 10 mols per mol of the transition metal compound used in the catalyst. The amount of electrophilic compound is normally 1 to 10000 mols, preferably 1 to 5000 mols per mol of the transition metal compound used in the catalyst.

What is very important in the present invention is that the halogenated metallocene compound is first reacted with the organometallic compound and the resultant product is then brought into contact with the ionic compound or the electrophilic compound. If this order is wrong, an obtained catalyst system cannot cause the polymerization of the  $\alpha$ -olefin at all, or even when the polymerization occurs, the activity of the catalyst system is very low, so that the reproducibility of the polymerization is poor. For example, as a technique which is utilized in the polymerization of the olefin by the use of a conventional Ziegler catalyst, there is a process in which a monomer or a solvent for use in the polymerization is treated with the organometallic compound, particularly an alkylaluminum compound in order to remove impurities contained in the monomer or the solvent therefrom, and this process is equal to the present invention in point of the employment of the alkylaluminum. With regard to the order of this conventional process, however, the metallocene compound is first brought into contact with a stable ion, and afterward the monomer and the solvent treated with the alkylaluminum are used. In this case, the alkylaluminum merely functions as a scavenger, and catalyst poisons are removed from the monomer and the solvent, with the result that the activity of the catalyst can be improved to some extent. However, this process is clearly different from that of the present invention, and thus the polymerization activity of the conventional catalyst is much lower than that of the catalyst system according to the present invention. Furthermore, in the case that the halogenated metallocene compound is replaced with an alkylated metallocene compound and the polymerization is carried out by the procedure of the present invention, the activity can be improved perceptibly, but this improved activity is still lower as compared with that of the present invention in which the halogenated metallocene compound is used. In a preferable embodiment of the present invention, the reaction product obtained by reacting the halogenated metallocene compound with the organometallic compound is brought into contact with the  $\alpha$ -olefin, prior to coming in contact with the compound which will be the stable anion. If the catalyst system which has been brought into contact with the  $\alpha$ -olefin and then done into contact with the compound which will be the stable anion is utilized, the polymerization makes smooth progress and the polymerization activity is also improved.

When the reaction product obtained by reacting the halogenated metallocene compound with the organometallic compound is brought into contact with the ionic compound or the electrophilic compound, this ionic compound or electrophilic compound can be divided into at least two portions and then added, instead of adding the total amount thereof at one time. This is also one embodiment of the present invention. That is, prior to the starting of the polymerization, a portion of the ionic compound or electrophilic compound is added, so that the polymerization is allowed to start, and after a suitable period of time, the remaining amount of the ionic compound or electrophilic compound is added during the polymerization, or alternatively the compound is successively added. This manner permits performing the polymerization stably for a long period of time.

For the purposes of enlarging the bulk density of the obtained polymer, improving the properties of the polymer powder and preventing the polymer from adhering to the polymerization vessel, the present invention suggests a polymerization method using a solid catalyst component in which the reaction product obtained by treating the halogenated metallocene compound with the organoaluminum compound is supported on a carrier. In this case, the contact treatment with the compound which will be the stable anion can be carried out under polymerization conditions or prior to the polymerization.

For the same purposes, a solid catalyst can be used in which the reaction product obtained by treating the halo-

generated metallocene compound with the organometallic compound and the ionic compound or electrophilic compound are both supported on a carrier. In this case, these compounds are required to be supported on the carrier which has been beforehand treated with the organometallic compound.

Examples of the carrier compound which can be used in the present invention include inorganic oxides such as 5 silica, alumina, silica-alumina, magnesia, silica-magnesia, boron oxide, titania and zirconia; various metallic salts such as inorganic halides, inorganic hydroxides, carbonates and perchlorates; and composites thereof. In addition, high-molecular compounds of a fine grain state which are organic compounds can also be used. The carrier compound, since preferably anhydrous, is required to be beforehand dried, if it is not what is industrially obtained. The drying of the carrier compound can usually be achieved by thermally treating the same in vacuo or under a dried inert gas at 10 100-1000°C, preferably 200-800°C for a predetermined period of time.

The size of the carrier compound which can be preferably utilized is usually such that its diameter is from 1 µm to 0.1 mm.

No particular restriction is put on a process for carrying, on the carrier, the reaction product obtained by treating the halogenated metallocene compound with the organoaluminum, and the carrying process can be achieved by bringing the treated reaction product into contact with the carrier compound in a solvent or a solid phase. In the case that they are contacted in a solvent, the carrier compound is first suspended in an inert solvent such as a hydrocarbon solvent, and the organometallic compound is then added thereto, followed by stirring. Examples of the solvent which can be used in this treatment include saturated hydrocarbon compounds such as propane, pentane, hexane, heptane, octane, nonane, decane, cyclopentane and cyclohexane; aromatic hydrocarbon compounds such as benzene, toluene and xylene; ether compounds such as diethyl ether and tetrahydrofuran; and ester compounds. In addition, in the case 15 the above-mentioned contact is carried out in the solid phase, the reaction product and the carrier compound are ground together. No particular restriction is put on the grinding manner, and the usual grinding technique using a ball mill, a vibration mill or the like can be directly employed. At this time, a grinding auxiliary can be used together, so long as it does not decompose the catalyst component under the grinding conditions.

20 In the case that the reaction product obtained by treating the halogenated metallocene compound with the organometallic compound as well as the ionic or electrophilic compound are both carried on the carrier, the carrier compound is required to be beforehand treated with the organometallic compound. No particular restriction is put on the manner of treating the carrier compound with the organometallic compound, and the treatment can be achieved by bringing the carrier compound into contact with the organometallic compound in a liquid phase or a solid phase. That is, the carrier compound is first suspended in an inert solvent such as a hydrocarbon compound, and the halogenated metallocene compound which has been treated with the organometallic compound is added to the suspension, followed by stirring, or alternatively both the components are ground together by the use of a mill such as a ball mill or a vibration mill.

25 In the case that the polymerization is carried out using this kind of carrier catalyst, it is also preferable to further use the organometallic compound together.

Furthermore, the compound which will be the stable anion may be beforehand brought into contact with a magnesium compound to form a solid catalyst component containing both the materials. Here, any magnesium compound can be used, so long as it does not react and inactivate the compound which will be the stable anion. Examples of the magnesium compound include salts such as magnesium chloride, magnesium bromide, magnesium iodide, magnesium oxide, magnesium perchlorate, magnesium hydroxide, magnesium carbonate and magnesium hydride; composite salts thereof; and composite-materials with metallic oxides such as silica, alumina and titania. The preferable size of these compounds is such that its diameter is from about 1 µm to 0.1 mm.

30 The magnesium compound in the present invention is preferably anhydrous, and it can be calcined prior to the contact with the compound which will be the stable anion, whereby at least free water may be preferably removed. No particular restriction is put on the manner of bringing the magnesium compound into contact with the compound which will be the stable anion to form a solid catalyst component, and the contact can be achieved in a solvent or a solid phase.

The manner of contacting them in the solvent comprises suspending the magnesium compound in an inert solvent such as a hydrocarbon solvent, and then adding the compound which will be the stable anion thereto, followed by stirring.

35 The contact manner in the solid phase comprises grinding the materials together. No particular restriction is put on the grinding way, and a usual way using a ball mill or a vibration mill can be directly employed. A grinding auxiliary such as an organic compound can be used together, so long as it does not decompose the catalyst component under the grinding conditions. Moreover, the together ground materials can be treated with a solvent. No particular restriction is put on a temperature in the grinding operation, but the grinding is usually carried out in the range of from -100 to 100°C, usually at a temperature in the vicinity of ordinary temperature.

40 In using the solid catalyst supported on the carrier in the polymerization of the  $\alpha$ -olefin of the present invention, it is preferred that the organometallic compound is additionally used, since the organometallic compound functions to remove impurities from the reaction solvent and the monomer. Examples of the organometallic compound are the same

as used in the treatment of the halogenated metallocene compound.

In the present invention, when the polymerization of the  $\alpha$ -olefin is carried out in the presence of an internal olefin, the molecular weight of the resultant polyolefin can be controlled. The internal olefin is preferably an unsaturated hydrocarbon having 4 to 20 carbon atoms represented by the following formula (VIII), (IX) or (X):

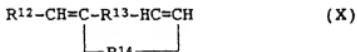
5



(wherein each of  $R^7$  and  $R^8$  is an alkyl hydrocarbon residue having 1 to 17 carbon atoms, and  $R^7$  and  $R^8$  may be bonded to each other to form a ring),

10 (wherein each of  $R^9$  and  $R^{11}$  is an alkyl hydrocarbon residue having 1 to 14 carbon atoms, and both may be bonded to each other to form a ring; and  $R^{10}$  is an alkylene hydrocarbon residue having 1 to 14 carbon atoms), and

15



(wherein each of  $R^{13}$  and  $R^{14}$  is an alkylene hydrocarbon residue having 1 to 14 carbon atoms; and  $R^{12}$  is an alkyl hydrocarbon residue having 1 to 14 carbon atoms).

20 Typical examples of the internal olefin include straight-chain internal olefins such as 2-butene, 2-pentene and 2-hexene; cyclic olefins such as cyclopentene, cyclohexene, cycloheptene and norbornene; and dienes such as 5-methylene-2-norbornene and 5-ethylidene norbornene. The amount of the internal olefin to be used depends upon the desired molecular weight of the polyolefin, but usually it is from 1/100000 to 1/10 of the monomer. When the molecular weight of the internal olefin is less than the above-mentioned range, the control of the molecular weight is not effective, and when it is larger than the above-mentioned range, the polymerization activity deteriorates noticeably, which is not practical.

25 Examples of the solvent which can be utilized in the preparation of the catalyst by the use of the catalyst component, the polymerization or the treatment include saturated hydrocarbons such as propane, butane, isobutane, pentane, hexane, heptane, octane, nonane, decane, cyclopentane, cyclohexane, cycloheptane and methylcyclohexane; aromatic hydrocarbon compounds such as benzene, toluene and xylene; and halogenated hydrocarbon compounds such as methylene chloride and chlorobenzene. In addition, ethers such as anisole and dimethylaniline as well as amines, nitriles and ester compounds having no active hydrogen can also be used as the solvents, so long as they neither link with nor strongly coordinate to a transition metal cation compound formed and inactivate its polymerization activity.

30 No particular restriction is put on conditions for the  $\alpha$ -olefin polymerization by the use of the catalyst component, and there can be utilized a solvent polymerization method using an inert medium, a mass polymerization method in which no inert medium is substantially present and a gaseous phase polymerization method. Examples of the  $\alpha$ -olefin which can be used in the polymerization include olefins having 2 to 25 carbon atoms, and typical examples thereof include straight-chain  $\alpha$ -olefins such as ethylene, propylene, butene-1, pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1, undecene-1, dodecene-1, tridecene-1, tetradecene-1, pentadecene-1, hexadecene-1 and octadecene-1; branched  $\alpha$ -olefins such as 3-methylbutene-1, 4-methylpentene-1 and 4,4-dimethylpentene-1; and cyclic olefins such as cyclopentene, cyclooctene and norbornene. These  $\alpha$ -olefins can be homopolymerized or mutually copolymerized, or if necessary, they can be copolymerized with a diene.

35 As a polymerization temperature and a polymerization pressure, there can be used such usual conditions as utilized in known methods, and the polymerization temperature is from -20 to 150°C, and the polymerization pressure is from the atmospheric pressure to 100 kg/cm<sup>2</sup>G.

40 Now, the present invention will be described in more detail in reference to examples.

#### Example 1

55 10 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was dissolved in 3 ml of deuterated benzene at room temperature, and 1 ml of the resultant solution was placed in an NMR tube and proton NMR was then measured. The measured results are shown in Fig. 1. Furthermore, 1 ml of the solution was poured into another NMR tube, and

4 mols of triethylaluminum per mol of zirconium was added thereto and proton NMR was then measured. Fig. 2 shows a spectrum of the proton NMR measured 10 minutes after the mixing. In the spectrum, the absorption of the original halogenated metallocene compound substantially disappeared, and a new absorption came out instead.

On the other hand, 10 mols of trimethylaluminum per mol of zirconium was added to 1 ml of the remaining solution.

Fig. 3 is a spectrum of proton NMR measured 10 minutes after the mixing. The absorption of the original halogenated metallocene compound clearly remains, and it is apparent that most of the metallocene compound remains unreacted. This mixture with trimethylaluminum was stored at room temperature for 240 hours, and the proton NMR was measured again. The results are shown in Fig. 4, but it is apparent that most of the halogenated metallocene compound remains unreacted even when the mixture was allowed to stand for a long period of time.

One liter of toluene was introduced into a 2-liter autoclave, and propylene was added until pressure has reached 3 kg/cm<sup>2</sup>G.

2 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was dissolved in 10 ml of toluene, and 43 mg of triethylaluminum was added thereto so that the amount of an aluminum atom might be 80 mols per mol of a zirconium atom, followed by mixing. After one minute had passed, 12.8 mg of triphenylmethanetetra(pentafluorophenyl)boron was added so that the amount of a boron atom might be 3 mols per mol of a zirconium atom, thereby forming a catalyst. Immediately, this catalyst was introduced into the above-mentioned autoclave and then stirred 20°C for 2 hours while a propylene pressure was maintained at 3 kg/cm<sup>2</sup>G. The contents were filtered and dried to obtain 91.8 g of a polymer. The amount of the thus produced polypropylene per gram of zirconium in the catalyst was 218 kg. According to 13C-NMR, the syndiotactic pentad fraction of the polymer was 0.88, and the intrinsic viscosity (hereinafter referred to as "η") of the polymer measured in a tetralin solution at 135°C was 1.14. The ratio of the weight average molecular weight to the number average molecular weight (hereinafter referred to as "MW/MN") of the polymer which was measured in 1,2,4-trichlorobenzene was 1.9.

#### Comparative Example 1

Fig. 5 shows the proton NMR of isopropyl(cyclopentadienyl-1-fluorenyl)zirconiumdimethyl complex obtained by methylating isopropyl(cyclopentadienyl-1-fluorenyl)-zirconium dichloride with methylolithium.

The polymerization of propylene was carried out by the same procedure as in Example 1 except that isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was replaced with 2 mg of the above-mentioned dimethyl complex. 30 Afterward, the contents were filtered and then dried at 60°C under 70 mmHg abs. for 8 hours to obtain 69 g of a white polypropylene powder. The amount of the produced polypropylene per gram of zirconium in the catalyst was 164 kg. The syndiotactic pentad fraction of the obtained polymer was 0.88, η was 1.13, and MW/MN was 2.2.

#### Comparative Example 2

35 The polymerization of propylene was carried out by the same procedure as in Example 1 except that no triethylaluminum was used, but a polymer was not obtained at all.

#### Comparative Example 3

40 A solution prepared by dissolving 2 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride in 10 ml of toluene was added to another solution prepared by dissolving 12.8 mg of triphenylmethanetetra(pentafluorophenyl) boron in 10 ml of toluene to form a catalyst component solution.

One liter of toluene was placed in a 2-liter autoclave, and 43 mg of triethylaluminum was added thereto. Next, 45 propylene was added until the pressure in the autoclave had reached 3 kg/cm<sup>2</sup>G, and after the temperature of the solution had been elevated up to 20°C, the above-mentioned catalyst component solution was added to the autoclave to start polymerization. Afterward, the polymerization of propylene was carried out by the same procedure as in Example 1, so that 0.8 g of a polymer was merely obtained.

#### Comparative Example 4

50 12.8 mg of triphenylmethanetetra(pentafluorophenyl)boron dissolved in 10 ml of toluene was added to a 2-liter autoclave containing 1 liter of toluene, and 43 mg of triethylaluminum was further added thereto. Next, propylene was added until pressure has reached 3 kg/cm<sup>2</sup>G, and after the temperature of the solution had been elevated up to 20°C, a solution prepared by dissolving 2 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride in 10 ml of toluene was added to the autoclave to start polymerization. Afterward, the polymerization of propylene was carried out by the same procedure as in Example 1, but a polymer was not obtained at all.

## Example 2

The polymerization of propylene was carried out by the same procedure as in Example 1 except that 2 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride and 43 mg of triethylaluminum were replaced with 10 mg of ethylenebis(tetrahydroindenyl)zirconium dichloride and 220 mg of triethylaluminum so that the amount of aluminum atom might be 80 mols per mol of the zirconium atom, thereby obtaining 60 g of a polymer. The amount of the produced polypropylene per gram of zirconium in the catalyst was 28.5 kg. The isotactic pentad fraction of the obtained polymer was 0.89,  $\eta$  was 0.72, and MW/MN was 2.3.

## Example 3

The polymerization of propylene was effected by the same procedure as in Example 1 except that 43 mg of triethylaluminum was replaced with 75 mg of triisobutylaluminum so that the amount of an aluminum atom might be 80 mols per mol of a zirconium atom, thereby obtaining 105 g of a polymer. In the obtained polymer,  $\eta$  was 1.18, an isotactic pentad fraction was 0.88, and MW/MN was 2.3.

## Example 4

The polymerization of propylene was effected by the same procedure as in Example 1 except that 12.8 mg of triphenylmethanetetra(pentafluorophenyl)boron was replaced with 25 mg of tri(pentafluorophenyl)boron (the amount of a boron atom was 9 mols per mol of a zirconium atom), thereby obtaining 56 g of a polymer. In the obtained polymer,  $\eta$  was 1.12, a syndiotactic pentad fraction was 0.86, and MW/MN was 2.3.

## Example 5

The polymerization of propylene was carried out by the same procedure as in Example 1 except that 43 mg of triethylaluminum was replaced with 28 mg of trimethylaluminum so that the amount of an aluminum atom might be 80 mols per mol of a zirconium atom, thereby only obtaining 1.8 g of a polymer. In the obtained polymer,  $\eta$  was 1.12, a syndiotactic pentad fraction was 0.87, and MW/MN was 2.2.

## Example 6

20 g of anhydrous magnesium chloride (made by Toho Titanium Co., Ltd., surface area 9 m<sup>2</sup>/g), 3.5 g of triphenylmethanetetra(pentafluorophenyl)boron and 4 ml of toluene were placed in a vibration mill (in which there was used a 1-liter grinding pot containing 300 steel balls having a diameter of 12 mm), followed by grinding for 17 hours. On the other hand, 4 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was dissolved in 10 ml of toluene, and 425 mg of triethylaluminum was added thereto so that the ratio of an aluminum atom to a zirconium atom might be 400, followed by mixing. The total amount of the resultant mixture solution and 592 mg of the above-mentioned ground material [which corresponded to 80 mg of triphenylmethanetetra(pentafluorophenyl)boron (the amount of a boron atom was 9.3 mols per mol of the zirconium atom)] were sufficiently dried and then placed under a nitrogen gas stream in a 5-liter autoclave in which the atmosphere was replaced with nitrogen. In addition, 1.5 kg of liquid propylene was added, and polymerization was carried out at 60°C for 1 hour. Unreacted propylene was purged from the system, and the contents were taken out and then dried to obtain 293 g of a polymer (which corresponded to 384 kg of polypropylene per gram of zirconium). According to 13C-NMR, a syndiotactic pentad fraction was 0.80,  $\eta$  was 0.68, and MW/MN was 5.0.

## Example 7

The polymerization of propylene was carried out by the same procedure as in Example 6 except that there was used a ground material obtained by replacing 3.5 g of triphenylmethanetetra(pentafluorophenyl)boron with 7 g of tri(pentafluorophenyl)boron (the amount of a boron atom was 30 mols per mol of a zirconium atom), thereby obtaining 123 g of a polymer. In the obtained polymer,  $\eta$  was 0.78, a syndiotactic pentad fraction was 0.80, and MW/MN was 3.0.

## Example 8

The polymerization of propylene was carried out by the same procedure as in Example 6 except that 4.0 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was replaced with 4.0 mg of ethylenebis(tetrahydroindenyl)-zirconium dichloride, thereby obtaining 246 g of a polymer. In the obtained polymer, an isotactic pentad fraction

was 0.80,  $\eta$  was 0.50, and MW/MN was 2.8.

Example 9

5 The polymerization of propylene was carried out by the same procedure as in Example 6 except that 425 mg of triethylaluminum was replaced with 740 mg of trisobutylaluminum so that the amount of an aluminum atom might be 400 mols per mol of a zirconium atom, thereby obtaining 351 g of a powder. In this powder,  $\eta$  was 0.88, a syndiotactic pentad fraction was 0.81, and MW/MN was 3.5.

10 Example 10

A mixture of 10 g of anhydrous magnesium chloride (made by Toho Titanium Co., Ltd., surface area 9  $\text{m}^2/\text{g}$ ) and 1.9 ml of a toluene solution containing 0.38 g of triethylaluminum was placed in a vibration mill (in which there was used a 1-liter grinding pot containing 300 steel balls having a diameter of 12 mm), followed by grinding for 17 hours. Furthermore, 2.2 g of triphenylmethanetetra(pentafluorophenyl)boron and a solution prepared by dissolving 0.4 g of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride in 2 g of a 20 weight % toluene solution of triethylaluminum (which corresponded to 0.4 g of triethylaluminum) were added to the vibration mill, followed by grinding for 4 hours. 200 mg of the ground material (which corresponded to 27 mg of triphenylmethanetetra(pentafluorophenyl)boron and 5.0 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride) and 230 mg of triethylaluminum were placed in a 5-liter autoclave. In addition, 1.5 kg of liquid propylene was added, and polymerization was then carried out at 60°C for 2 hours. Unreacted propylene was purged from the system, and the contents were taken out and then dried to obtain 265 g of a polymer (which corresponded to 252 kg of polypropylene per gram of zirconium). According to  $^{13}\text{C}$ -NMR, a syndiotactic pentad fraction was 0.80,  $\eta$  was 0.79, and MW/MN was 2.5.

25 Example 11

The same procedure as in Example 10 was effected except that 2.2 g of triphenylmethanetetra(pentafluorophenyl) boron was replaced with 2.4 g of tri(pentafluorophenyl)boron, to synthesize a solid catalyst. The polymerization of propylene was then carried out using 200 mg of this solid catalyst [which corresponded to 29 mg of tri(pentafluorophenyl)boron and 5.0 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride] and 230 mg of triethylaluminum, thereby obtaining 106 g of a powder. In this powder,  $\eta$  was 0.79, a syndiotactic pentad fraction was 0.78, and MW/MN was 2.7. In addition, bulk specific gravity was 0.30 g/ml, and the adhesion of the polymer to the wall of the polymerizer was slight.

35 Example 12

The same procedure as in Example 10 was effected except that 0.4 g of isopropyl(cyclopentadienyl-1-fluorenyl) zirconium dichloride was replaced with 0.4 g of ethylenebis(tetrahydroindenyl)zirconium dichloride, to synthesize a solid catalyst. The polymerization of propylene was then carried out using 200 mg of this solid catalyst [which corresponded to 27 mg of triphenylmethanetetra(pentafluorophenyl)boron and 5.0 mg of ethylenebis-(tetrahydroindenyl) zirconium dichloride] and 230 mg of triethylaluminum, thereby obtaining 215 g of a powder. In this powder,  $\eta$  was 0.49, an isotactic pentad fraction was 0.81, and MW/MN was 3.5. In addition, bulk specific gravity was 0.31 g/ml, and the adhesion of the polymer to the wall of the polymerizer was slight.

45 Example 13

The polymerization of propylene was carried out by the same procedure as in Example 6 except that triethylaluminum was replaced with trisobutylaluminum so that the molar ratio of aluminum to zirconium might be unchanged, thereby obtaining 308 g of a powder. In this powder,  $\eta$  was 0.80, a syndiotactic pentad fraction was 0.81, and MW/MN was 2.5. In addition, bulk specific gravity was 0.32 g/ml, and the adhesion of the polymer to the wall of the polymerizer was slight.

Example 14

55 50 g of  $\gamma$ -alumina which had been treated at 800°C under reduced pressure for 6 hours was placed in a 2000-ml four-necked flask in which the atmosphere had been replaced with nitrogen, and 1000 ml of toluene was further added thereto. In addition, 25 ml of a toluene solution containing 5.0 g of trimethylaluminum was added dropwise, while the contents were stirred. After the stirring at room temperature for 17 hours, the treated alumina was filtered through a

glass filter, washed with 50 ml of pentane three times, and then dried under reduced pressure. Afterward, 10 g of  $\gamma$ -alumina which had been treated with trimethylaluminum was placed in a 2000-ml four-necked flask in which the atmosphere had been replaced with nitrogen, and 100 ml of toluene was further added thereto. Afterward, 2.2 g of triphenylmethanetetra(pentafluorophenyl)boron and a solution prepared by dissolving 0.2 g of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride in 2 g of a 20 wt.% triethylaluminum solution in toluene (which corresponded to 0.4 g of triethylaluminum) were added dropwise, while the contents were stirred. After stirring at room temperature for 1 hour, the solvent was distilled off under reduced pressure, and the residue was washed with 50 ml of pentane three times and then dried under reduced pressure. 200 mg of this treated material (which corresponded to 34 mg of triphenylmethanetetra(pentafluorophenyl)boron and 3.1 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride) and 230 mg of triethylaluminum were placed in a 5-liter autoclave. In addition, 1.5 kg of liquid propylene was added, and polymerization was then carried out at 60°C for 2 hours. Unreacted propylene was purged from the system, and the contents were taken out and then dried to obtain 220 g of a polymer (which corresponded to 337 kg of polypropylene per gram of zirconium). According to  $^{13}\text{C-NMR}$ , a syndiotactic pentad fraction was 0.80,  $\eta$  was 0.79, and MW/MN was 2.6. In addition, bulk specific gravity was 0.32 g/ml, and the adhesion of the polymer to the wall of the polymerizer was slight.

#### Example 15

1.5 mg of isopropyl(cyclopentadienyl-1-fluorenyl)-zirconium dichloride was dissolved in 10 ml of toluene, and 78 mg of triethylaluminum was added thereto, thereby forming a catalyst. Next, 1 liter of toluene was added to a 2-liter autoclave, and the above-mentioned catalyst was then introduced thereto. Propylene was further added so that the pressure might be 3 kg/cm<sup>2</sup>G at 20°C, and a solution prepared by dissolving 6.42 mg of triphenylmethanetetra(pentafluorophenyl)boron in 10 ml of toluene was added with the aid of a propylene gas under pressure, and polymerization was then carried out at 20°C while a pressure of 3 kg/cm<sup>2</sup>G was maintained. After the polymerization had been done for 60 minutes, a solution prepared by dissolving 6.42 mg of triphenylmethanetetra(pentafluorophenyl)boron in 10 ml of toluene was introduced thereto with the aid of a propylene gas under pressure, and the polymerization was then carried out for 60 minutes. In this polymerization, any vigorous reaction was not observed, and temperature was controlled easily. Next, filtration and drying followed to obtain 121 g of a polymer (which corresponded to 382 kg of polypropylene per gram of zirconium). According to  $^{13}\text{C-NMR}$ , a syndiotactic pentad fraction was 0.88,  $\eta$  was 1.21, and MW/MN was 2.2.

#### Example 16

The polymerization of propylene was carried out by the same procedure as in Example 15 except that the total amount of 12.8 mg of triphenylmethanetetra(pentafluorophenyl)boron at an early stage in Example 15 was added at one time and the same compound was not added any more. In this case, immediately after triphenylmethanetetra(pentafluorophenyl)boron had been added, vigorous reaction occurred, but after the polymerization had been carried out for 60 minutes, the absorption of propylene was scarcely observed. The polymerization was further continued for 60 minutes, and filtration and drying followed to obtain 93.7 g of a polymer (which corresponded to 296 kg of polypropylene per gram of zirconium). According to  $^{13}\text{C-NMR}$ , a syndiotactic pentad fraction was 0.87,  $\eta$  was 1.16, and MW/MN was 2.1.

#### Example 17

Polymerization was carried out by the same procedure as in Example 15 except that 2 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride and 78 mg of triethylaluminum were used and that a solution prepared by dissolving 10.7 mg of triphenylmethanetetra(pentafluorophenyl)boron in 40 ml of toluene was used as much as the amount of 1/4 thereof at an early stage and after the start of the polymerization, the solution was used in an amount of 1/4 thereof every 30 minutes. In this polymerization, any vigorous reaction was not observed, the absorption of propylene was constant. After the polymerization had been done for 2 hours, filtration and drying followed to obtain 129 g of a polymer (which corresponded to 306 kg of polypropylene per gram of zirconium). According to  $^{13}\text{C-NMR}$ , a syndiotactic pentad fraction was 0.90,  $\eta$  was 1.10, and MW/MN was 2.3.

#### Example 18

Polymerization was carried out by the same procedure as in Example 15 except that in place of triphenylmethanetetra(pentafluorophenyl)boron, tri(pentafluorophenyl)boron was used in an amount of 10 mg at an early stage and in an amount of 15 mg after 60 minutes. After the polymerization, filtration and drying followed to obtain 61 g of a powder

(which corresponded to 193 kg of polypropylene per gram of zirconium). In the powder,  $\eta$  was 1.15, a syndiotactic pentad fraction was 0.87, and MW/MN was 2.2.

Example 19

5 10 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was dissolved in 10 ml of toluene, and 215 mg of triethylaluminum was added thereto so that the amount of an aluminum atom might be 80 mols per mol of a zirconium atom, followed by mixing. Afterward, 1/5 of the resultant mixture as a catalyst was placed in a 2-liter autoclave containing 1 liter of toluene. Next, propylene was added so that the pressure might be 3 kg/cm<sup>2</sup>G, and a solution prepared by dissolving 9.7 mg of triphenylmethanetetra(pentafluorophenyl)boron in 10 ml of toluene was then added to the autoclave so that the amount of a boron atom might be 2.3 mols per mol of a zirconium atom. While the propylene pressure was maintained at 3 kg/cm<sup>2</sup>G, the contents were stirred at 20°C for 2 hours. The contents were filtered and dried to obtain 159.6 g of a polymer. The amount of the produced polypropylene per gram of zirconium in the catalyst was 379 kg. According to 13C-NMR, a syndiotactic pentad fraction of the polymer was 0.89,  $\eta$  was 1.21, and MW/MN was 2.0.

10 15 Next, a toluene solution of the above-mentioned isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride and triethylaluminum was stored at room temperature for one month, and the polymerization of propylene was then carried out in like manner. After the polymerization, filtration and drying followed to obtain 161 g of a powder (which corresponded to 382 kg of polypropylene per gram of zirconium). In the powder,  $\eta$  was 1.20, a syndiotactic pentad fraction was 0.88, and MW/MN was 2.1. Even after the storage, the performance of the polymerization did not change.

Comparative Example 5

25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000 1005 1010 1015 1020 1025 1030 1035 1040 1045 1050 1055 1060 1065 1070 1075 1080 1085 1090 1095 1100 1105 1110 1115 1120 1125 1130 1135 1140 1145 1150 1155 1160 1165 1170 1175 1180 1185 1190 1195 1200 1205 1210 1215 1220 1225 1230 1235 1240 1245 1250 1255 1260 1265 1270 1275 1280 1285 1290 1295 1300 1305 1310 1315 1320 1325 1330 1335 1340 1345 1350 1355 1360 1365 1370 1375 1380 1385 1390 1395 1400 1405 1410 1415 1420 1425 1430 1435 1440 1445 1450 1455 1460 1465 1470 1475 1480 1485 1490 1495 1500 1505 1510 1515 1520 1525 1530 1535 1540 1545 1550 1555 1560 1565 1570 1575 1580 1585 1590 1595 1600 1605 1610 1615 1620 1625 1630 1635 1640 1645 1650 1655 1660 1665 1670 1675 1680 1685 1690 1695 1700 1705 1710 1715 1720 1725 1730 1735 1740 1745 1750 1755 1760 1765 1770 1775 1780 1785 1790 1795 1800 1805 1810 1815 1820 1825 1830 1835 1840 1845 1850 1855 1860 1865 1870 1875 1880 1885 1890 1895 1900 1905 1910 1915 1920 1925 1930 1935 1940 1945 1950 1955 1960 1965 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015 2020 2025 2030 2035 2040 2045 2050 2055 2060 2065 2070 2075 2080 2085 2090 2095 2100 2105 2110 2115 2120 2125 2130 2135 2140 2145 2150 2155 2160 2165 2170 2175 2180 2185 2190 2195 2200 2205 2210 2215 2220 2225 2230 2235 2240 2245 2250 2255 2260 2265 2270 2275 2280 2285 2290 2295 2300 2305 2310 2315 2320 2325 2330 2335 2340 2345 2350 2355 2360 2365 2370 2375 2380 2385 2390 2395 2400 2405 2410 2415 2420 2425 2430 2435 2440 2445 2450 2455 2460 2465 2470 2475 2480 2485 2490 2495 2500 2505 2510 2515 2520 2525 2530 2535 2540 2545 2550 2555 2560 2565 2570 2575 2580 2585 2590 2595 2600 2605 2610 2615 2620 2625 2630 2635 2640 2645 2650 2655 2660 2665 2670 2675 2680 2685 2690 2695 2700 2705 2710 2715 2720 2725 2730 2735 2740 2745 2750 2755 2760 2765 2770 2775 2780 2785 2790 2795 2800 2805 2810 2815 2820 2825 2830 2835 2840 2845 2850 2855 2860 2865 2870 2875 2880 2885 2890 2895 2900 2905 2910 2915 2920 2925 2930 2935 2940 2945 2950 2955 2960 2965 2970 2975 2980 2985 2990 2995 3000 3005 3010 3015 3020 3025 3030 3035 3040 3045 3050 3055 3060 3065 3070 3075 3080 3085 3090 3095 3100 3105 3110 3115 3120 3125 3130 3135 3140 3145 3150 3155 3160 3165 3170 3175 3180 3185 3190 3195 3200 3205 3210 3215 3220 3225 3230 3235 3240 3245 3250 3255 3260 3265 3270 3275 3280 3285 3290 3295 3300 3305 3310 3315 3320 3325 3330 3335 3340 3345 3350 3355 3360 3365 3370 3375 3380 3385 3390 3395 3400 3405 3410 3415 3420 3425 3430 3435 3440 3445 3450 3455 3460 3465 3470 3475 3480 3485 3490 3495 3500 3505 3510 3515 3520 3525 3530 3535 3540 3545 3550 3555 3560 3565 3570 3575 3580 3585 3590 3595 3600 3605 3610 3615 3620 3625 3630 3635 3640 3645 3650 3655 3660 3665 3670 3675 3680 3685 3690 3695 3700 3705 3710 3715 3720 3725 3730 3735 3740 3745 3750 3755 3760 3765 3770 3775 3780 3785 3790 3795 3800 3805 3810 3815 3820 3825 3830 3835 3840 3845 3850 3855 3860 3865 3870 3875 3880 3885 3890 3895 3900 3905 3910 3915 3920 3925 3930 3935 3940 3945 3950 3955 3960 3965 3970 3975 3980 3985 3990 3995 4000 4005 4010 4015 4020 4025 4030 4035 4040 4045 4050 4055 4060 4065 4070 4075 4080 4085 4090 4095 4100 4105 4110 4115 4120 4125 4130 4135 4140 4145 4150 4155 4160 4165 4170 4175 4180 4185 4190 4195 4200 4205 4210 4215 4220 4225 4230 4235 4240 4245 4250 4255 4260 4265 4270 4275 4280 4285 4290 4295 4300 4305 4310 4315 4320 4325 4330 4335 4340 4345 4350 4355 4360 4365 4370 4375 4380 4385 4390 4395 4400 4405 4410 4415 4420 4425 4430 4435 4440 4445 4450 4455 4460 4465 4470 4475 4480 4485 4490 4495 4500 4505 4510 4515 4520 4525 4530 4535 4540 4545 4550 4555 4560 4565 4570 4575 4580 4585 4590 4595 4600 4605 4610 4615 4620 4625 4630 4635 4640 4645 4650 4655 4660 4665 4670 4675 4680 4685 4690 4695 4700 4705 4710 4715 4720 4725 4730 4735 4740 4745 4750 4755 4760 4765 4770 4775 4780 4785 4790 4795 4800 4805 4810 4815 4820 4825 4830 4835 4840 4845 4850 4855 4860 4865 4870 4875 4880 4885 4890 4895 4900 4905 4910 4915 4920 4925 4930 4935 4940 4945 4950 4955 4960 4965 4970 4975 4980 4985 4990 4995 5000 5005 5010 5015 5020 5025 5030 5035 5040 5045 5050 5055 5060 5065 5070 5075 5080 5085 5090 5095 5100 5105 5110 5115 5120 5125 5130 5135 5140 5145 5150 5155 5160 5165 5170 5175 5180 5185 5190 5195 5200 5205 5210 5215 5220 5225 5230 5235 5240 5245 5250 5255 5260 5265 5270 5275 5280 5285 5290 5295 5300 5305 5310 5315 5320 5325 5330 5335 5340 5345 5350 5355 5360 5365 5370 5375 5380 5385 5390 5395 5400 5405 5410 5415 5420 5425 5430 5435 5440 5445 5450 5455 5460 5465 5470 5475 5480 5485 5490 5495 5500 5505 5510 5515 5520 5525 5530 5535 5540 5545 5550 5555 5560 5565 5570 5575 5580 5585 5590 5595 5600 5605 5610 5615 5620 5625 5630 5635 5640 5645 5650 5655 5660 5665 5670 5675 5680 5685 5690 5695 5700 5705 5710 5715 5720 5725 5730 5735 5740 5745 5750 5755 5760 5765 5770 5775 5780 5785 5790 5795 5800 5805 5810 5815 5820 5825 5830 5835 5840 5845 5850 5855 5860 5865 5870 5875 5880 5885 5890 5895 5900 5905 5910 5915 5920 5925 5930 5935 5940 5945 5950 5955 5960 5965 5970 5975 5980 5985 5990 5995 6000 6005 6010 6015 6020 6025 6030 6035 6040 6045 6050 6055 6060 6065 6070 6075 6080 6085 6090 6095 6100 6105 6110 6115 6120 6125 6130 6135 6140 6145 6150 6155 6160 6165 6170 6175 6180 6185 6190 6195 6200 6205 6210 6215 6220 6225 6230 6235 6240 6245 6250 6255 6260 6265 6270 6275 6280 6285 6290 6295 6300 6305 6310 6315 6320 6325 6330 6335 6340 6345 6350 6355 6360 6365 6370 6375 6380 6385 6390 6395 6400 6405 6410 6415 6420 6425 6430 6435 6440 6445 6450 6455 6460 6465 6470 6475 6480 6485 6490 6495 6500 6505 6510 6515 6520 6525 6530 6535 6540 6545 6550 6555 6560 6565 6570 6575 6580 6585 6590 6595 6600 6605 6610 6615 6620 6625 6630 6635 6640 6645 6650 6655 6660 6665 6670 6675 6680 6685 6690 6695 6700 6705 6710 6715 6720 6725 6730 6735 6740 6745 6750 6755 6760 6765 6770 6775 6780 6785 6790 6795 6800 6805 6810 6815 6820 6825 6830 6835 6840 6845 6850 6855 6860 6865 6870 6875 6880 6885 6890 6895 6900 6905 6910 6915 6920 6925 6930 6935 6940 6945 6950 6955 6960 6965 6970 6975 6980 6985 6990 6995 7000 7005 7010 7015 7020 7025 7030 7035 7040 7045 7050 7055 7060 7065 7070 7075 7080 7085 7090 7095 7100 7105 7110 7115 7120 7125 7130 7135 7140 7145 7150 7155 7160 7165 7170 7175 7180 7185 7190 7195 7200 7205 7210 7215 7220 7225 7230 7235 7240 7245 7250 7255 7260 7265 7270 7275 7280 7285 7290 7295 7300 7305 7310 7315 7320 7325 7330 7335 7340 7345 7350 7355 7360 7365 7370 7375 7380 7385 7390 7395 7400 7405 7410 7415 7420 7425 7430 7435 7440 7445 7450 7455 7460 7465 7470 7475 7480 7485 7490 7495 7500 7505 7510 7515 7520 7525 7530 7535 7540 7545 7550 7555 7560 7565 7570 7575 7580 7585 7590 7595 7600 7605 7610 7615 7620 7625 7630 7635 7640 7645 7650 7655 7660 7665 7670 7675 7680 7685 7690 7695 7700 7705 7710 7715 7720 7725 7730 7735 7740 7745 7750 7755 7760 7765 7770 7775 7780 7785 7790 7795 7800 7805 7810 7815 7820 7825 7830 7835 7840 7845 7850 7855 7860 7865 7870 7875 7880 7885 7890 7895 7900 7905 7910 7915 7920 7925 7930 7935 7940 7945 7950 7955 7960 7965 7970 7975 7980 7985 7990 7995 8000 8005 8010 8015 8020 8025 8030 8035 8040 8045 8050 8055 8060 8065 8070 8075 8080 8085 8090 8095 8100 8105 8110 8115 8120 8125 8130 8135 8140 8145 8150 8155 8160 8165 8170 8175 8180 8185 8190 8195 8200 8205 8210 8215 8220 8225 8230 8235 8240 8245 8250 8255 8260 8265 8270 8275 8280 8285 8290 8295 8300 8305 8310 8315 8320 8325 8330 8335 8340 8345 8350 8355 8360 8365 8370 8375 8380 8385 8390 8395 8400 8405 8410 8415 8420 8425 8430 8435 8440 8445 8450 8455 8460 8465 8470 8475 8480 8485 8490 8495 8500 8505 8510 8515 8520 8525 8530 8535 8540 8545 8550 8555 8560 8565 8570 8575 8580 8585 8590 8595 8600 8605 8610 8615 8620 8625 8630 8635 8640 8645 8650 8655 8660 8665 8670 8675 8680 8685 8690 8695 8700 8705 8710 8715 8720 8725 8730 8735 8740 8745 8750 8755 8760 8765 8770 8775 8780 8785 8790 8795 8800 8805 8810 8815 8820 8825 8830 8835 8840 8845 8850 8855 8860 8865 8870 8875 8880 8885 8890 8895 8900 8905 8910 8915 8920 8925 8930 8935 8940 8945 8950 8955 8960 8965 8970 8975 8980 8985 8990 8995 9000 9005 9010 9015 9020 9025 9030 9035 9040 9045 9050 9055 9060 9065 9070 9075 9080 9085 9090 9095 9100 9105 9110 9115 9120 9125 9130 9135 9140 9145 9150 9155 9160 9165 9170 9175 9180 9185 9190 9195 9200 9205 9210 9215 9220 9225 9230 9235 9240 9245 9250 9255 9260 9265 9270 9275 9280 9285 9290 9295 9300 9305 9310 9315 9320 9325 9330 9335 9340 9345 9350 9355 9360 9365 9370 9375 9380 9385 9390 9395 9400 9405 9410 9415 9420 9425 9430 9435 9440 9445 9450 9455 9460 9465 9470 9475 9480 9485 9490 9495 9500 9505 9510 9515 9520 9525 9530 9535 9540 9545 9550 9555 9560 9565 9570 9575 9580 9585 9590 9595 9600 9605 9610 9615 9620 9625 9630 9635 9640 9645 9650 9655 9660 9665 9670 9675 9680 9685 9690 9695 9700 9705 9710 9715 9720 9725 9730 9735 9740 9745 9750 9755 9760 9765 9770 9775 9780 9785 9790 9795 9800 9805 9810 9815 9820 9825 9830 9835 9840 9845 9850 9855 9860 9865 9870 9875 9880 9885 9890 9895 9900 9905 9910 9915 9920 9925 9930 9935 9940 9945 9950 9955 9960 9965 9970 9975 9980 9985 9990 9995 9999

The same procedure as in Example 19 was effected except that in place of triethylaluminum, 375 mg of triisobutylaluminum was stored at room temperature for one month, and the polymerization of propylene was then carried out in like manner.

laluminum was used so that the amount of an aluminum atom might be 80 mols per mol of a zirconium atom, thereby preparing a catalyst solution, and the polymerization of propylene was then carried out to obtain 193 g of a polymer. In the powder,  $\eta$  was 1.17, a syndiotactic pentad fraction was 0.88, and MW/MN was 2.1.

The above-mentioned toluene solution of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride and triisobutylaluminum was stored at room temperature for one month, and the polymerization of propylene was then carried out in like manner. In this case, the activity of the polymerization scarcely changed.

#### Example 22

The same procedure as in Example 19 was effected except that toluene was replaced with cyclohexane as a solvent to prepare a catalyst solution, and the polymerization of propylene was then carried out to obtain 70 g of a polymer. In the polymer,  $\eta$  was 1.41, a syndiotactic pentad fraction was 0.87, and MW/MN was 2.2. The above-mentioned cyclohexane solution of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride and triethylaluminum was stored at room temperature for one month, and the polymerization of propylene was then carried out in like manner. In this case, the activity of the polymerization scarcely changed.

#### Example 23

15 ml of a cyclohexane solution containing 6.64 g of triethylaluminum was added to 2.2 g of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride. After the solution was stirred at room temperature for 24 hours, it was cooled to -78°C and further allowed to stand for 24 hours. This solution was filtered through a glass filter to remove a small amount of insolubles, with the result that a uniform mixture solution was obtained.

5 g of  $\gamma$ -alumina which had been thermally treated at 600°C for 6 hours under reduced pressure was placed in a 200-ml four-necked flask in which the atmosphere had been replaced with nitrogen, and 25 ml of toluene was further added and, while the contents were stirred, 5 ml of the above-mentioned reaction mixture solution was added dropwise thereto. After the stirring at room temperature for 24 hours, the treated alumina was filtered through a glass filter, washed with 50 ml of pentane three times, and then dried under reduced pressure. The soluble components which had not been carried on the  $\gamma$ -alumina were removed, and the remaining insolubles were further washed with 50 ml of pentane three times, and then dried under reduced pressure to obtain a solid catalyst component. 100 mg of this solid catalyst component [which corresponded to 3 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride], 80 mg of triphenylmethanetetra(pentyl)boron and 400 mg of triethylaluminum were placed in a 5-liter autoclave whose interior had been sufficiently dried and replaced with nitrogen. Next, 1.5 kg of liquid propylene was added thereto, and the contents were heated up to 60°C and polymerization was continued for one hour.

Unreacted propylene was purged from the system, and the contents were taken out and then dried at 60°C under 700 mmHg for 8 hours to obtain 183 g of a powder (which corresponded to 290 kg of polypropylene per gram of zirconium). According to 13C-NMR, a syndiotactic pentad fraction was 0.80,  $\eta$  was 0.78, and MW/MN was 2.1. In addition, bulk specific gravity was 0.27 g/ml, and the adhesion of the polymer to the wall of the polymerizer was slight.

#### Example 24

The same procedure as in Example 23 was effected except that isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was replaced with 1.95 g of ethylenobis-(tetrahydroindenyl)zirconium dichloride, to synthesize a solid catalyst component, and the polymerization of propylene was then carried out to obtain 98.6 g of a powder. According to 13C-NMR, an isotactic pentad fraction was 0.80,  $\eta$  was 0.40, and MW/MN was 2.3. In addition, bulk specific gravity was 0.24 g/ml, and the adhesion of the polymer to the wall of the polymerizer was slight.

#### Example 25

The polymerization of propylene was carried out by the same procedure as in Example 23 except that in place of triethylaluminum, triisobutylaluminum was used so that the amount of an aluminum atom might be 80 mols per mol of a zirconium atom, thereby obtaining 195 g of a polymer. In the powder,  $\eta$  was 0.76, a syndiotactic pentad fraction was 0.81, and MW/MN was 2.6. In addition, bulk specific gravity was 0.24 g/ml, and the adhesion of the polymer to the wall of the polymerizer was slight.

#### Example 26

40 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was dissolved in 10 ml of toluene, and 0.86 g of triethylaluminum was further added thereto. 1 g of alumina (Aerosilaluminum Oxide-L, made by Nippon Aerosil

Inc., surface area 95.8 m<sup>2</sup>/g) which had been thermally treated at 1000°C under reduced pressure was added thereto to form a catalyst. Next, under a nitrogen gas stream, the catalyst component was placed in a 5-liter autoclave which had been sufficiently dried and the atmosphere of which had been replaced with nitrogen, and 1.5 kg of liquid propylene was further added thereto. The contents were then heated up to 50°C and polymerization was continued for 2 hours. 5 Unreacted propylene was purged, and the contents were taken out and then dried at 60°C under 70 mmHg for 8 hours to obtain 15 g of a white polypropylene powder (which corresponded to 1.6 kg of polypropylene per gram of zirconium). According to 13C-NMR, a syndiotactic pentad fraction was 0.73,  $\eta$  was 0.46, and MW/MN was 2.6.

## Example 27

10 The same alumina as used in Example 26 was thermally treated at 200°C, and it was then reacted with triethylaluminum (in an amount of 1 g to 10 g of aluminum) in a toluene solvent. The soluble components were removed by filtration with a glass filter, and the residue was washed with toluene twice and then dried under reduced pressure. The same polymerization as in Example 26 was carried out except that 1 g of this alumina was used, thereby obtaining 35 15 g of a polymer (which corresponded to 4.2 kg of polypropylene per gram of zirconium). According to 13C-NMR, a syndiotactic pentad fraction was 0.78,  $\eta$  was 0.66, and MW/MN was 2.5.

## Comparative Example 6

20 Polymerization was carried out by the same procedure as in Example 26 except that  $\alpha$ -alumina having a surface area of 10 m<sup>2</sup>/g was used, thereby obtaining 1 g of a polymer (which corresponded to 0.1 kg of polypropylene per gram of zirconium). According to 13C-NMR, a syndiotactic pentad fraction was 0.75,  $\eta$  was 0.42, and MW/MN was 2.7.

## Comparative Example 7

25 Polymerization was carried out by the same procedure as in Example 26 except that any triethylaluminum was not used, but a polymer was not obtained at all.

## Example 28

30 The polymerization of propylene was carried out by the same procedure as in Example 26 except that isopropyl (cyclopentadienyl-1-fluorenyl)zirconium dichloride was replaced with 10 mg of ethylenebis(tetrahydroindenyl)zirconium dichloride and 0.22 g of triethylaluminum was used, thereby obtaining 16 g of a polymer (which corresponded to 7.5 kg of polypropylene per gram of zirconium). According to 13C-NMR, an isotactic pentad fraction was 0.72,  $\eta$  was 0.42, 35 and MW/MN was 2.6.

## Example 29

40 The polymerization of butene-1 was carried out by the same procedure as in Example 25 except that 50 g of butene-1 was placed in a 300-milliliter autoclave instead of propylene and a polymerization time was 6 hours, thereby obtaining 7.2 g of a polymer. According to 13C-NMR, a syndiotactic pentad fraction was 0.79,  $\eta$  was 0.20, and MW/MN was 2.2.

## Example 30

45 40 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was dissolved in 10 ml of toluene, and 0.86 g of triethylaluminum was further added thereto. In addition, 2 g of anhydrous magnesium chloride (made by Toho Titanium Co., Ltd., surface area 9 m<sup>2</sup>/g) was added thereto, thereby forming a catalyst component. Next, under a nitrogen gas stream, the catalyst component was placed in a 5-liter autoclave which had been sufficiently dried and the atmosphere of which had been replaced with nitrogen, and 1.5 kg of liquid propylene was further added thereto. The contents were then heated up to 50°C and polymerization was continued for 2 hours. Unreacted propylene was purged, and the contents were taken out and then dried at 60°C under 70 mmHg for 8 hours to obtain 10 g of a white polypropylene powder (which corresponded to 1.2 kg of polypropylene per gram of zirconium). According to 13C-NMR, a syndiotactic pentad fraction was 0.79,  $\eta$  was 0.43, and MW/MN was 2.5.

## Comparative Example 8

55 Polymerization was carried out by the same procedure as in Example 30 except that any triethylaluminum was

not used, but a polymer was not obtained at all.

Example 31

5 The polymerization of propylene was carried out by the same procedure as in Example 30 except that isopropyl (cyclopentadienyl-1-fluorenyl)zirconium dichloride was replaced with 10 mg of ethylenebis(tetrahydroindenyl)zirconium dichloride and 0.22 g of triethylaluminum was used, thereby obtaining 6 g of a polymer (which corresponded to 0.7 kg of polypropylene per gram of zirconium). According to 13C-NMR, an isotactic pentad fraction was 0.86,  $\eta$  was 0.52, and MW/MN was 2.4.

10

Example 32

Under a nitrogen atmosphere, 20 g of magnesium chloride (made by Toho Titanium Co., Ltd., surface area 9 m<sup>2</sup>/g) and 4 ml of a toluene were placed in a 1-liter grinding pot containing 300 steel balls having a diameter of 12 mm, followed by grinding for 39 hours. The surface area of the ground material was 110 m<sup>2</sup>/g.

15 40 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was dissolved in 10 ml of toluene, and 0.86 g of triethylaluminum was further added thereto. In addition, 2 g of the above-mentioned ground magnesium compound was added, thereby forming a catalyst component. Next, under a nitrogen gas stream, the catalyst component was placed in a 5-liter autoclave which had been sufficiently dried and the atmosphere of which had been replaced with nitrogen, and 1.5 kg of liquid propylene was added thereto. The contents were then heated up to 50°C and polymerization was carried out for 2 hours. Unreacted propylene was purged, and the contents were taken out and then dried at 60°C under 70 mmHg for 8 hours to obtain 156 g of a white polypropylene powder (which corresponded to 18.5 kg of polypropylene per gram of zirconium). According to 13C-NMR, a syndiotactic pentad fraction was 0.78,  $\eta$  was 0.66, and MW/MN was 2.5.

20

Example 33

25 20 g of anhydrous magnesium chloride (made by Toho Titanium Co., Ltd., surface area 9 m<sup>2</sup>/g), 2 g of diphenyldimethoxysilane and 3 ml of decane were placed in a grinding pot, followed by grinding for 34 hours in accordance with the same procedure as in Example 32. The surface area of the ground material was 172 m<sup>2</sup>/g.

30 Polymerization was carried out by the same procedure as in Example 32 except that 2 g of this ground magnesium compound was used, to obtain 70 g of a white polypropylene powder (which corresponded to 8.3 kg of polypropylene per gram of zirconium). According to 13C-NMR, a syndiotactic pentad fraction was 0.78,  $\eta$  was 0.66, and MW/MN was 2.5.

35

Example 34

40 The polymerization of propylene was carried out by the same procedure as in Example 32 except that isopropyl (cyclopentadienyl-1-fluorenyl)zirconium dichloride was replaced with 10 mg of ethylenebis(tetrahydroindenyl)zirconium dichloride and 0.22 g of triethylaluminum was used, thereby obtaining 160 g of a polymer (which corresponded to 72.7 kg of polypropylene per gram of zirconium).  $\eta$  of the polymer was 0.38, an isotactic pentad fraction was 0.82, and MW/MN was 2.6.

45

Example 35

45 Diphenyldimethoxysilane was replaced with 1.50 g of triethylaluminum, and the grinding as above was conducted. The surface area of the ground material was 107 m<sup>2</sup>/g. Polymerization was then carried out using this ground material by the same procedure as in Example 32 to obtain 155 g of a polymer.  $\eta$  of the polymer was 0.61, a syndiotactic pentad fraction was 0.81, and MW/MN was 2.6.

50

Example 36

55 40 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was dissolved in 10 ml of toluene, and 19.5 ml of an n-heptane solution containing 2.32 g of n-butyylethylmagnesium (trade name MAGALA BEM, made by Toso Akzo Co., Ltd.) was added. Next, under a nitrogen gas stream, the resultant mixture was placed in a 5-liter autoclave which had been sufficiently dried and the atmosphere of which had been replaced with nitrogen, and 1.5 kg of liquid propylene was added thereto. Furthermore, 34.9 ml of a toluene solution containing 5.06 g of diethylaluminum chloride was added thereto, and the contents were then heated up to 60°C and polymerization was carried out for 2 hours.

Unreacted propylene was purged, and the contents were taken out and then dried at 60°C under 70 mmHg for 8 hours to obtain 172 g of a white polypropylene powder. According to 13C-NMR, a syndiotactic pentad fraction was 0.78,  $\eta$  was 0.65, and MW/MN was 2.2.

5 Example 37

Polymerization was carried out by the same procedure as in Example 36 except that isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was replaced with dimethylsilyl(isobutyl)cyclopentadienylzirconium dichloride, thereby obtaining 33.6 g of a polymer.  $\eta$  of the polymer was 0.25, an isotactic pentad fraction was 0.89, and MW/MN was 2.3.

Example 38

One liter of toluene and 0.75 ml of norbornene were placed in a 2-liter autoclave, and there was further added, to the autoclave, a product obtained by reacting, in a toluene solvent, 2 mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride and 43 mg of triethylaluminum so that the amount of an aluminum atom might be 80 mols per mol of a zirconium atom. Next, propylene was added so that the pressure in the autoclave might be 3 kg/cm<sup>2</sup>G, and a solution prepared by dissolving 9.5 mg of triphenylmethanetetra(pentafluorophenyl)boron in 10 ml of toluene was then added to the autoclave so that the amount of a boron atom might be 2.2 mols per mol of the zirconium atom. While the propylene pressure was maintained at 3 kg/cm<sup>2</sup>G, the contents were stirred at 20°C for 2 hours. The contents were filtered and dried to obtain 105 g of a polymer. According to 13C-NMR, the polymer had a syndiotactic pentad fraction of 0.89,  $\eta$  of 0.93, and MW/MN of 2.2. The ash content in the polymer was 275 ppm.

Comparative Example 9

Polymerization was carried out by the same procedure as in Example 38 except that triethylaluminum was replaced with 1.34 g of methylaluminoxane (made by Toso Akzo Co., Ltd., polymerization degree 16.1) and triphenylmethanetetra(pentafluorophenyl)boron was not used, thereby obtaining 102 g of a polymer.  $\eta$  of the polymer was 1.10, a syndiotactic pentad fraction was 0.92, and MW/MN was 2.2. The ash content in the polymer was 10620 ppm.

30 Example 39

The same procedure as in Example 38 was effected except that in polymerization, 1.0 ml of norbornene was used, thereby obtaining 80 g of a polymer. According to 13C-NMR, a syndiotactic pentad fraction of the polymer was 0.89,  $\eta$  was 0.82, and MW/MN was 2.1.

Example 40

The same procedure as in Example 38 was effected except that in polymerization, 1.5 ml of norbornene was used, thereby obtaining 53 g of a polymer. According to 13C-NMR, the polymer had a syndiotactic pentad fraction of 0.89,  $\eta$  of 0.73, and MW/MN of 2.2.

Example 41

45 One mg of dimethylsilyl(isobutyl)cyclopentadienylzirconium dichloride was dissolved in 10 ml of toluene, and 23 mg of triethylaluminum was added thereto so that the amount of an aluminum atom might be 80 mols per mol of a zirconium atom, thereby forming a catalyst component. This catalyst component was placed in an autoclave containing 1 liter of toluene. Next, propylene was added so that the pressure in the autoclave might be 3 kg/cm<sup>2</sup>G, and a solution prepared by dissolving 5.1 mg of triphenylmethanetetra(pentafluorophenyl)boron in 10 ml of toluene was then added to the autoclave so that the amount of a boron atom might be 2.2 mols per mol of the zirconium atom. While the propylene pressure was maintained at 3 kg/cm<sup>2</sup>G, the contents were stirred at 20°C for 2 hours. The contents were filtered and dried to obtain 156 g of a polymer (which corresponded to 690 kg of polypropylene per gram of zirconium). According to 13C-NMR, an isotactic pentad fraction of the polymer was 0.97,  $\eta$  was 1.02, and MW/MN was 2.4. The ash content in the polymer was 100 ppm.

55 Comparative Example 10

The polymerization of propylene was carried out by the same procedure as in Example 41 except that triethylalu-

5  
minum was replaced with 0.27 g of methylaluminoxane (made by Toso Akzo Co., Ltd., polymerization degree 16.1) and triphenylmethanetetra(pentafluorophenyl)boron was not used, thereby obtaining 35 g of a polymer (which corresponded to 155 kg of polypropylene per gram of zirconium).  $\eta$  of the polymer was 1.46, an isotactic pentad fraction was 0.96, and MW/MN was 2.4. The ash content in the polymer was 5500 ppm.

#### Example 42

10 In place of dimethylsilyl(bis(2,4-dimethylcyclopentadienyl)zirconium dichloride, 2 mg of dimethylsilyl(bis(2,3,5-trimethylcyclopentadienyl)zirconium dichloride and 40 mg of triethylaluminum were dissolved in 10 ml of toluene to form a catalyst component, and this catalyst component was placed in an autoclave containing 1 liter of toluene. Next, propylene was added so that the pressure in the autoclave might be 3 kg/cm<sup>2</sup>G, and the same procedure as in Example 41 was effected except that a solution prepared by dissolving 10 mg of triphenylmethanetetra(pentafluorophenyl)boron in 10 ml of toluene was then added to the autoclave, thereby obtaining 47 g of a polymer (which corresponded to 108 kg of polypropylene per gram of zirconium).  $\eta$  of the polymer was 1.52, an isotactic pentad fraction was 0.98, and MW/MN was 2.4.

#### Comparative Example 11

20 The polymerization of propylene was carried out by the same procedure as in Example 41 except the following steps. A solution prepared by dissolving 9.5 mg of triphenylmethanetetra(pentafluorophenyl)boron in 10 ml of toluene was added to another solution prepared by dissolving 2 mg of dimethylsilyl(bis(2,4-dimethylcyclopentadienyl)zirconium dichloride in 10 ml of toluene to form a catalyst component, and 1 liter of toluene was then placed in a 2-liter autoclave. Furthermore, 46 mg of triethylaluminum was added and the above-mentioned catalyst component was then added thereto, thereby obtaining 5 g of a polymer (which corresponded to 11 kg of polypropylene per gram of zirconium).  $\eta$  of the polymer was 0.98, an isotactic pentad fraction was 0.97, and MW/MN was 2.3.

#### Comparative Example 12

30 The polymerization of propylene was carried out by the same procedure as in Example 41 except the following steps. 9.5 mg of triphenylmethanetetra(pentafluorophenyl) boron was dissolved in 10 ml of toluene, and 46 mg of triethylaluminum was added thereto. The resultant mixture was placed in a 2-liter autoclave containing 1 liter of toluene. Next, propylene was added so that the pressure might be 3 kg/cm<sup>2</sup>G, and a solution prepared by dissolving 2 mg of dimethylsilyl(bis(2,4-dimethylcyclopentadienyl)zirconium dichloride in 10 ml of toluene was added to the autoclave. In this case, a polymer was not obtained at all.

#### Example 43

40 The polymerization of propylene was carried out by the same procedure as in Example 41 except that triethylaluminum was replaced with triisobutylaluminum so that the molar ratio of aluminum to zirconium might be unchanged, thereby obtaining 188 g of a powder.  $\eta$  of this powder was 1.20, an isotactic pentad fraction was 0.98, and MW/MN was 2.3.

#### Example 44

45 The polymerization of propylene was carried out by the same procedure as in Example 41 except that triphenylmethanetetra(pentafluorophenyl)boron was replaced with 10.8 mg of tri(pentafluorophenyl)boron, thereby obtaining 56 g of a powder.  $\eta$  of this powder was 1.01, an isotactic pentad fraction was 0.96, and MW/MN was 2.4.

#### Example 45

50 Two mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was dissolved in 10 ml of toluene, and 75 mg of triisobutylaluminum was added thereto so that the amount of an aluminum atom might be 80 mols per mol of a zirconium atom, followed by mixing. The resultant mixture was placed in a 2-liter autoclave containing 1 liter of toluene. Next, propylene was added so that the pressure might be 3 kg/cm<sup>2</sup>G, and a solution prepared by dissolving 9.5 mg of triphenylmethanetetra(pentafluorophenyl)boron in 10 ml of toluene was then added to the autoclave so that the amount of a boron atom might be 2.2 mols per mol of the zirconium atom. While the propylene pressure was maintained at 3 kg/cm<sup>2</sup>G, the contents were stirred at 20°C for 2 hours. The contents were filtered and dried to obtain 193 g of a polymer. The amount of the produced polypropylene per gram of zirconium in the catalyst was 458 kg. According to

13C-NMR, a syndiotactic pentad fraction of the polymer was 0.89,  $\eta$  was 1.17, and MW/MN was 2.1.

On the other hand, for the comparison with the above-mentioned results, the following operation was made.

Two mg of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride was dissolved in 10 ml of toluene, and 75 mg of triisobutylaluminum was added thereto and then mixed. Furthermore, a solution prepared by dissolving 9.5 mg of triphenylmethanetetra(pentafluorophenyl)boron in 10 ml of toluene was then added thereto, thereby obtaining a catalyst component.

Next, this catalyst component was placed in a 2-liter autoclave containing 1 liter of toluene. Propylene was then added so that the pressure might be 3 kg/cm<sup>2</sup>G, followed by stirring at 20°C for 2 hours. The contents were filtered and dried to obtain 29.4 g of a polymer. The amount of the produced polypropylene per gram of zirconium in the catalyst was 68 kg. According to 13C-NMR, a syndiotactic pentad fraction of the polymer was 0.88,  $\eta$  was 1.16, and MW/MN was 2.2.

It can be understood from the foregoing that when the reaction product of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride and triisobutylaluminum is brought into contact with propylene prior to the contact with triphenylmethanetetra(pentafluorophenyl)boron, polymerization activity can be remarkably improved.

15

#### Example 46

The polymerization of propylene was carried out by the same procedure as in Example 45 except that triisobutylaluminum was replaced with 43 mg of triethylaluminum so that the molar ratio of aluminum to zirconium might be unchanged and triphenylmethanetetra(pentafluorophenyl)boron was replaced with 9.7 mg of triphenylmethanetetra(pentafluorophenyl)aluminum so that the molar ratio of the aluminum atom to the zirconium atom was equal to that of a boron atom to the zirconium atom, thereby obtaining 160 g of a powder. The amount of the produced polypropylene per gram of zirconium in the catalyst was 380 kg. According to 13C-NMR, a syndiotactic pentad fraction of the polymer was 0.91,  $\eta$  was 1.24, and MW/MN was 2.0.

26

#### Example 47

The polymerization of propylene was carried out by the same procedure as in Example 45 except that triisobutylaluminum was replaced with 43 mg of triethylaluminum so that the molar ratio of aluminum to zirconium might be unchanged and triphenylmethanetetra(pentafluorophenyl)boron was replaced with 10.1 mg of triphenylmethanetetra(pentafluorophenyl)gallium so that the molar ratio of a gallium atom to the zirconium atom was equal to that of a boron atom to the zirconium atom, thereby obtaining 184 g of a powder. The amount of the produced polypropylene per gram of zirconium in the catalyst was 437 kg. According to 13C-NMR, a syndiotactic pentad fraction of the polymer was 0.91,  $\eta$  was 1.22, and MW/MN was 2.0.

35

#### Example 48

The polymerization of propylene was carried out by the same procedure as in Example 45 except the following steps. Two mg of isopropyl(cyclopentadienyl-1-fluorenyl)-zirconium dichloride was dissolved in 10 ml of toluene, and in place of triisobutylaluminum, an n-heptane solution containing 10.2 mg of n-butyethylmagnesium (trade name MAGALA BEM, made by Toso Akzo Co., Ltd.) was added thereto, thereby forming a catalyst component. Afterward, 32 mg of triethylaluminum was placed in a 2-liter autoclave containing 1 liter of toluene, and the above-mentioned catalyst component was added to the autoclave, thereby obtaining 116 g of a powder. The amount of the produced polypropylene per gram of zirconium in the catalyst was 275 kg. According to 13C-NMR, the polymer had a syndiotactic pentad fraction of 0.89,  $\eta$  of 1.07, and MW/MN of 2.2.

On the other hand, for the comparison with the above-mentioned results, the polymerization of propylene was carried out in the same manner as described above except that n-butyethylmagnesium was not used. In this case, 2 g of a polymer was merely obtained.

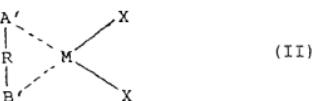
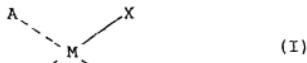
50

#### Example 49

The polymerization of propylene was carried out by the same procedure as in Example 45 except the following steps. Two mg of isopropyl(cyclopentadienyl-1-fluorenyl)-zirconium dichloride was dissolved in 10 ml of toluene, and in place of triisobutylaluminum, a n-heptane solution containing 11.4 mg of diethylzinc was added thereto and then mixed to form a catalyst component. 32 mg of triethylaluminum was placed in a 2-liter autoclave containing 1 liter of toluene, and the above-mentioned catalyst component was further added to the autoclave, thereby obtaining 22.7 g of a powder. The amount of the produced polypropylene per gram of zirconium in the catalyst was 54 kg. According to 13C-NMR, the polymer had a syndiotactic pentad fraction of 0.88,  $\eta$  of 1.14, and MW/MN of 2.1.

## Claims

1. A method for polymerizing an  $\alpha$ -olefin characterized by bringing the  $\alpha$ -olefin into contact with a catalyst which is obtained by reacting a halogenated metallocene compound with an organometallic compound, and then bringing the resultant reaction product into contact with an ionic compound or an electrophilic compound, wherein the halogenated metallocene compound is a compound represented by the formula (I) or (II)



(wherein A and B or A' and B' are mutually identical or different and are unsaturated hydrocarbon residues coordinated to a central atom; R is a divalent straight-chain hydrocarbon residue which may have a side chain, or a residue in which a part or all of the carbon atoms of the straight-chain may be substituted by silicon atoms, germanium atoms or tin atoms; X is a halogen atom; and M is a titanium atom, a zirconium atom or a hafnium atom); the organometallic compound is triethylaluminum, tripropylaluminum, triisopropylaluminum, tributylaluminum, triisobutylaluminum, tripentylaluminum, trimethylaluminum, triheptylaluminum, trioctylaluminum, tridecylaluminum, isopropylaluminum, diethylaluminum hydride, diisopropylaluminum hydride, diisobutylaluminum hydride, diethylzinc, diphenylzinc, divinylzinc, dimethylmagnesium, diethylmagnesium, dibutylmagnesium, dihexylmagnesium or butylethylmagnesium; the ionic compound is represented by the formula (V)



(wherein Q is a cationic component of the ionic compound, and is selected from carbonium cation, tropylium cation, ammonium cation, oxonium cation, sulfonium cation and phosphonium cation, silver ion, gold ion, platinum ion, copper ion, palladium ion, mercury ion and ferrocenium ion, and Y is an anionic component of the ionic compound selected from the anionic components of an ionic organoboron, organoaluminum, organogallium, organophosphorus, organoarsenic and organoantimony); and the electrophilic compound comprises magnesium halides or inorganic oxides.

45

2. The method of claim 1, wherein the ionic compound or the electrophilic compound is a solid catalyst component obtained by beforehand bringing the compound into contact with magnesium chloride.

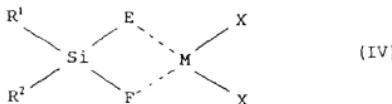
3. The method of claim 1, wherein the ionic compound or the electrophilic compound is divided into at least two portions and then added to the system in which the  $\alpha$ -olefin is being subjected to polymerization by the contact with the catalyst.

50

4. The method of claim 1, wherein the ionic compound or the electrophilic compound is brought into contact with the reaction product of the metallocene compound and the organometallic compound, said reaction product having been supported on a carrier prior to the contact with the ionic compound or the electrophilic compound.

55

5. The method of claim 1, wherein the halogenated metallocene compound is a compound represented by the formula (IV)



(wherein each of E and F is a di- or tri-substituted cyclopentadienyl group having a hydrocarbon residue having 1 to 10 carbon atoms, a silyl group or a halogen atom as a substituent; R<sup>1</sup> and R<sup>2</sup> may be identical or different and bonded to silicon which is linked with the two cyclopentadienyl groups, and each of R<sup>1</sup> and R<sup>2</sup> is a hydrogen atom or a hydrocarbon residue having 1 to 10 carbon atoms; X is a halogen atom; and M is a titanium atom, a zirconium atom or a hafnium atom).

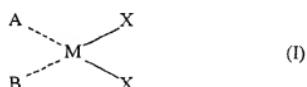
10 6. The method of claim 1, wherein the electrophilic compound is water-free aluminum oxide having a specific surface area of from 15 to 500 m<sup>2</sup>/g.

7. The method of claim 1, wherein the electrophilic compound is a magnesium halide having a specific surface area of from 1 to 300 m<sup>2</sup>/g.

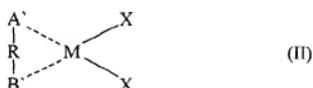
20

**Patentansprüche**

25 1. Verfahren zum Polymerisieren eines  $\alpha$ -Olefins, dadurch gekennzeichnet, daß das  $\alpha$ -Olefin mit einem Katalysator in Kontakt gebracht wird, der erhalten wird, indem eine halogenierte Metallocenverbindung mit einer metallorganischen Verbindung zur Reaktion gebracht wird und dann das resultierende Reaktionsprodukt mit einer ionischen Verbindung oder einer elektrophilen Verbindung in Kontakt gebracht wird, wobei die halogenierte Metallocenverbindung eine Verbindung ist, die durch die Formeln (I) oder (II)



35



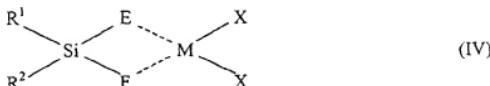
45 50 wiedergegeben wird (wobei A und B oder A' und B' jeweils identisch oder verschieden sind und ungesättigte Kohlenwasserstoffreste sind, die an ein zentrales Atom koordinativ angelagert sind, R ein zweiwertiger Rest aus einer linearen Kohlenwasserstoffkette ist, der eine Seitenkette aufweisen kann oder einen Rest, in dem ein Teil der oder alle Kohlenstoffatome der linearen Kette durch Siliciumatome, Germaniumatome oder Zinnatome substituiert sein können, X ein Halogenatom ist und M ein Titanatom, ein Zirkoniumatom oder ein Hafniumatom ist), wobei die metallorganische Verbindung Triethylaluminium, Tripropylaluminium, Triisopropylaluminium, Tributylaluminium, Triisobutylaluminium, Tripentylaluminium, Trihexylaluminium, Triheptylaluminium, Trioctylaluminium, Tridecylaluminium, Isopropylaluminium, Diethylaluminumhydrid, Diisopropylaluminumhydrid, Diisobutylaluminumhydrid, Diethylzink, Diphenylzink, Divinylzink, Dimethylmagnesium, Diethylmagnesium, Dibutylmagnesium, Dihexylmagnesium oder Butylethylmagnesium ist, die ionische Verbindung durch die Formel (V)

55



wiedergegeben wird (wobei Q ein kationische Bestandteil der ionischen Verbindung ist und aus Kohlenstoffkation, Tropylum-Kation, Ammoniumkation, Oxoniumkation, Sulfoniumkation und Phosphoniumkation, Silberion, Goldion, Platinerion, Palladiumion, Quecksilberion und Ferroceniumkation ausgewählt ist und Y ein anionischer Bestandteil der ionischen Verbindung ist, der aus anionischen bororganischen, aluminiumorganischen, galliumorganischen, phosphororganischen, arsenorganischen und antimonorganischen Verbindungen ausgewählt ist) und die elektrophile Verbindung Magnesiumhalogenide oder anorganische Oxide aufweist.

2. Verfahren nach Anspruch 1, wobei die ionische Verbindung oder die elektrophile Verbindung ein fester Katalysatorbestandteil sind, der erhalten wird, indem zuvor die Verbindung in Kontakt mit Magnesiumchlorid gebracht wird.
3. Verfahren nach Anspruch 1, wobei die ionische Verbindung oder die elektrophile Verbindung in zwei Teile aufgeteilt werden und dann dem System zugegeben werden, in dem das  $\alpha$ -Olefin einer Polymerisation unterzogen wird, indem sie in Kontakt mit dem Katalysator gebracht wird.
4. Verfahren nach Anspruch 1, wobei die ionische Verbindung oder die elektrophile Verbindung mit der Metallocenverbindung und der metallorganischen Verbindung in Kontakt gebracht wird, wobei das Reaktionsprodukt, bevor es mit der ionischen Verbindung oder der elektrophilen Verbindung in Kontakt gebracht wird, auf einen Träger aufgebracht wird.
5. Verfahren nach Anspruch 1, wobei die halogenierte Metallocenverbindung eine Verbindung ist, die durch die Formel (IV)



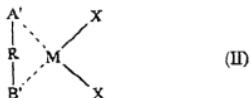
wiedergegeben wird (wobei jedes von E und F eine di- oder tri-substituierte Cyclopentadienylgruppe mit einem Kohlenwasserstoffrest von 1 bis 10 Kohlenstoffatomen, einer Silylgruppe oder einem Halogenatom als Substituenten ist, R<sup>1</sup> und R<sup>2</sup> gleich oder verschieden sein können und an Silicium gebunden sind, das mit den beiden Cyclopentadienylgruppen verknüpft ist und jeder R<sup>1</sup> und R<sup>2</sup> ein Wasserstoffatom oder ein Kohlenwasserstoffrest mit 1 bis 10 Kohlenstoffatomen ist, X ein Halogenatom ist und M ein Titanatom, ein Zirkoniumatom oder ein Hafniumatom ist).

6. Verfahren nach Anspruch 1, wobei die elektrophile Verbindung wasserfreies Aluminiumoxid mit einer spezifischen Oberfläche von 15 bis 500 m<sup>2</sup>/g ist.
7. Verfahren nach Anspruch 1, wobei die elektrophile Verbindung ein Magnesiumhalogenid mit einer spezifischen Oberfläche von 1 bis 300 m<sup>2</sup>/g ist.

#### Revendications

1. Procédé de polymérisation d'une  $\alpha$ -oléfine, caractérisé en ce que l'on met l' $\alpha$ -oléfine en contact avec un catalyseur obtenu par réaction d'un composé de métallocène halogéné avec un composé organométallique, puis mise en contact du produit de réaction obtenu avec un composé ionique ou un composé électrophile, le composé de métallocène halogéné étant un composé représenté par la formule (I) ou (II)





(dans lesquelles A et B ou A' et B' sont identiques ou différents les uns des autres et représentent des résidus hydrocarbonés insaturés coordonnés à un atome central; R est un résidu hydrocarboné divalent qui peut avoir une chaîne latérale, ou un résidu dans lequel les atomes de carbone de la chaîne linéaire peuvent être tous ou en partie remplacés par des atomes de silicium, des atomes de germanium ou des atomes d'étain; X est un atome d'halogène, et M est un atome de titane, un atome de zirconium ou un atome de hafnium); le composé organométallique étant le triéthylaluminium, le tripropylaluminium, le trisopropylaluminium, le tributylaluminium, le trisobutylaluminium, le triptyaluminium, le trihexylaluminium, le triheptyaluminium, le trioctylaluminium, le tridécytaluminium, l'isoprénylaluminium, l'hydure de diéthylaluminium, l'hydure de diisopropylaluminium, l'hydure de diisobutylaluminium, le diéthylzinc, le diphenylzinc, le divinylzinc, le diméthylmagnésium, le diéthylmagnésium, le dibutylmagnésium, le dihexylmagnésium ou le butyléthylmagnésium; le composé ionique étant représenté par la formule (V)

20

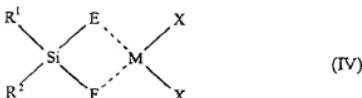


25 (dans laquelle Q est le constituant cationique du composé ionique et est choisi parmi un cation carbonium, un cation tropylium, un cation ammonium, un cation oxonium, un cation sulfonium et un cation phosphonium, un ion d'argent, un ion d'or, un ion de platine, un ion de cuivre, un ion de palladium, un ion de mercure et un ion ferrocénium, et Y est le constituant anionique du composé ionique, choisi parmi les constituants anioniques d'un composé ionique d'organobore, organoaluminium, organogallium, organophosphore, organoarsenic et organoantimoïne); et le composé électrophile comprenant des halogénures de magnésium ou des oxydes inorganiques.

30

2. Procédé selon la revendication 1, dans lequel le composé ionique ou le composé électrophile est un constituant de catalyseur solide obtenu par mise en contact préalable du composé avec du chlorure de magnésium.
3. Procédé selon la revendication 1, dans lequel on divise le composé ionique ou le composé électrophile en au moins deux portions puis on l'ajoute au système dans lequel l'α-oléfine est soumise à une polymérisation par contact avec le catalyseur.
4. Procédé selon la revendication 1, dans lequel on met le composé ionique ou le composé électrophile en contact avec le produit de réaction du composé métallocène et du composé organométallique, ledit produit de réaction ayant été immobilisé sur un support avant sa mise en contact avec le composé ionique ou le composé électrophile.
5. Procédé selon la revendication 1, dans lequel le composé métallocène halogéné est un composé représenté par la formule (IV)

45



(dans laquelle chacun des E et F est un groupe cyclopentadiényle di- ou trisubstitué ayant comme substituant un résidu hydrocarboné de 1 à 10 atomes de carbone, un groupe silyle ou un atome d'halogène; R' et R'' peuvent être identiques ou différents et sont liés au silicium qui est lié aux deux groupes cyclopentadiényle, et chacun des R' et R'' est un atome d'hydrogène ou un résidu hydrocarboné de 1 à 10 atomes de carbone; X est un atome d'halogène; et M est un atome de titane, un atome de zirconium ou un atome de hafnium).

55

6. Procédé selon la revendication 1, dans lequel le composé électrophile est un oxyde d'aluminium anhydre ayant une surface spécifique de 15 à 500 m<sup>2</sup>/g.
- 5 7. Procédé selon la revendication 1, dans lequel le composé électrophile est un halogénure de magnésium ayant une surface spécifique de 1 à 300 m<sup>2</sup>/g.

10

15

20

25

30

35

40

45

50

55

Fig. 1

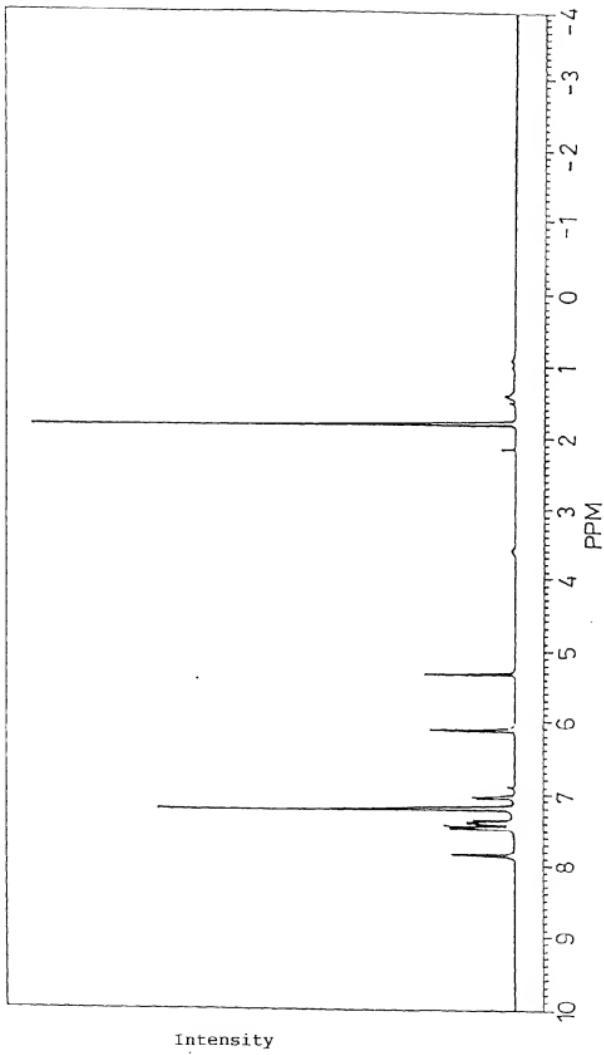
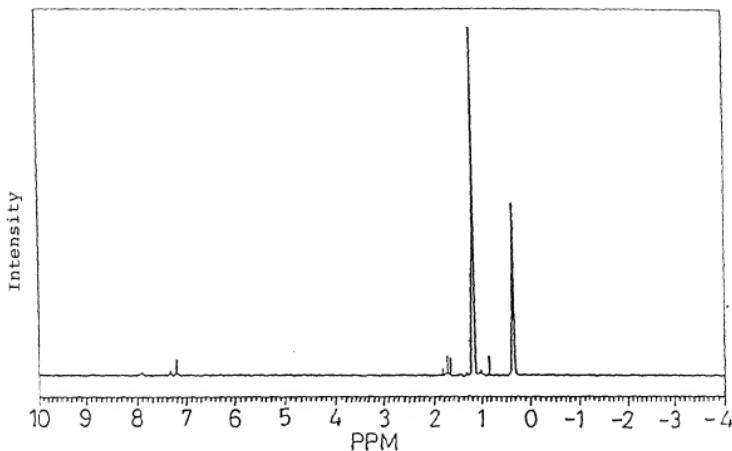


Fig. 2

(a)



(b)

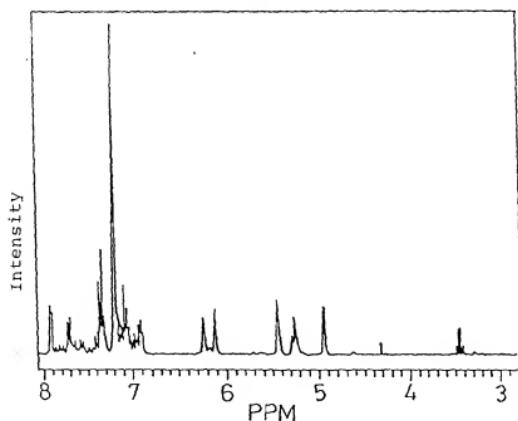


Fig. 3

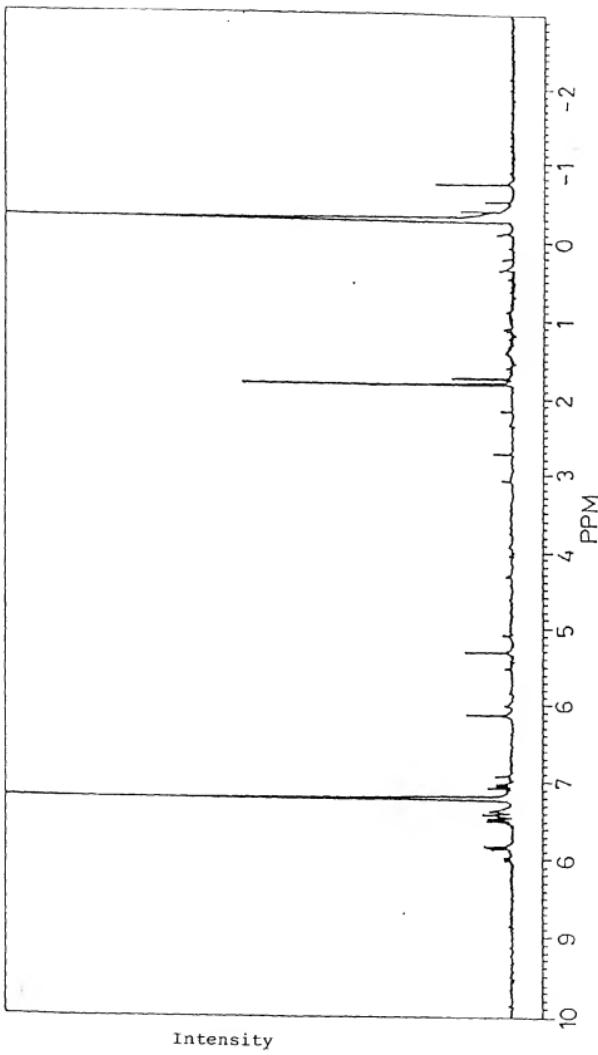


Fig. 4

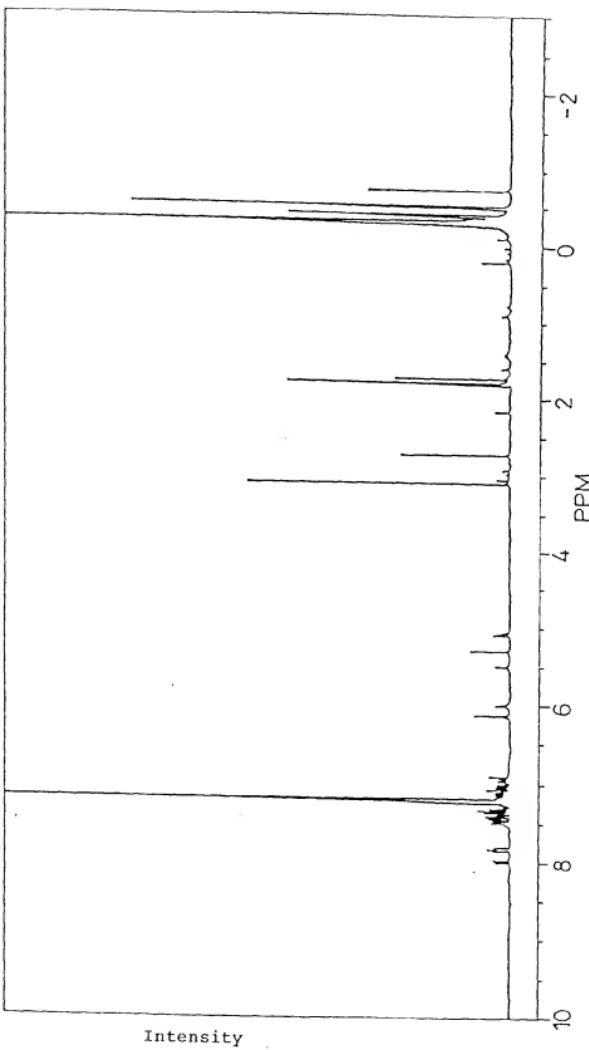


Fig. 5

